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# An Introduction to Statistical Physics for Students

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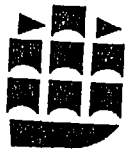

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# *Preface*

This book represents an attempt to give an introduction to statistical physics in a form which is suitable for final year undergraduate students. No claim of originality is made for either the content or the mode of presentation but the material has been chosen in order to emphasize the basic methods of statistical physics and those results which are of particular importance for physicists. The applications of statistical physics which have been given, both in the text and as problems, have been chosen to illustrate the methods of statistical mechanics and statistical thermodynamics rather than to provide a comprehensive survey of these applications.

The basis of the text is a course of lectures given by the author to final year physics students for the external degree of the University of London. The treatment given has, however, been extended to take account of some of the variations in the physics courses on statistical mechanics and statistical thermodynamics of some other universities. Partly for this reason the concepts of the canonical and the grand canonical ensemble have been introduced although these also demonstrate the generality of the statistical method in the treatment of physical problems.

It has been felt that the extension of the methods of statistical physics to fields such as chemical equilibria and semiconductors is best left to those works which deal with the particular field in detail. For the more advanced applications, and also for general reading, the student is referred to the Bibliography given on p. 170 to which the author makes a general acknowledgement for the use of various data which has been included in the present work. The author also wishes to thank Dr R. C. Lloyd-Jenkins for many useful discussions, Mr R. G. F. Taylor for reading the rough manuscript and Miss V. S. Gay for converting it into a readable form.

A.J.P.

Chapter 1

# Introduction

## 1.1. *The scope of statistical physics*

There are many cases in the study of physics where an exact treatment of the properties of a given physical system is rendered impracticable because of the large number of components involved. As an example of such a case consider the behaviour of the molecules in a gas. At standard temperature and pressure one cubic centimetre of a gas will contain about $2 \times 10^{19}$ molecules. It would be theoretically possible to write down all the classical equations of motion of these molecules provided that their positions and velocities at some instant of time, and the factors determining their energies, are known. These equations and the calculation of the subsequent motion of the gas molecules would not, however, be very rewarding even if they could be interpreted from the volume of paper which they would occupy. Because of this it is the purpose of statistical physics to enable the macroscopic properties of such a gas to be described in terms of the microscopic* properties of the molecules without involving the detailed calculation of the motions of the individual molecules.

In any experimental measurement which may be performed on the gas the result obtained will, in general, be an average value of some mechanical or thermodynamic property of the gas such as the pressure or the temperature. (The averaging in these cases will involve the smoothing-out of fluctuations over the period of the measurement and over the different regions of the gas.) The most detailed measurement likely to be made on the gas molecules, in practice, is one which would involve the distribution of the molecular velocities over the range of values from zero to infinity. It therefore follows from both theoretical and experimental considerations that any useful study of the behaviour of the gas will have to be made with the aid of statistical methods.

* In this context 'microscopic' implies small scale, or atomic scale, as opposed to macroscopic or large scale and does not imply any connection with the optical (or electron) microscope.

The student will already be acquainted with one possible treatment of the average properties of a gas through the application of classical thermodynamics. However, the very generality of the first and second laws of thermodynamics restricts the information which may be obtained from their application. It will thus be seen necessary to subject the gas to a more detailed statistical analysis if further information about the nature of the gas, and about thermodynamic properties in general, is required.

The considerations which have been applied in the above discussion for the case of a gas will also apply in a variety of other cases. Obvious examples are the 'gas' of photons which exists in the electromagnetic radiation inside a constant temperature enclosure, the 'gas' of electrons inside a metallic conductor and also the vibrating atoms in a crystal lattice since, in each case, there are a large number of individual components to be considered. It will be seen that, because of these large numbers of components, the statistical calculation of the properties of the systems will give values very close to the values which are obtained experimentally. It will also be seen that, although the large number of components involved cannot be treated exactly, this very complexity leads to important regularities in the thermodynamic properties, e.g. the temperature and the entropy, of the system. (Because the macroscopic properties which are predicted by the application of statistical physics frequently involve these thermodynamic quantities the whole subject is often referred to as 'statistical thermodynamics'. For the purpose of the present work, however, the term statistical thermodynamics will be reserved for those cases where the macroscopic thermodynamic properties are specifically considered.)

In order to obtain statistical results for the mechanical and thermodynamic properties of the systems under consideration it will, of course, be necessary to introduce certain assumptions as a basis for the theory. However, while the assumptions may be presented as being both reasonable and fundamental, the student should be aware that their only proper justification lies in the agreement which exists between the resulting theoretical predictions and experiment.

Finally, it is noted that, besides predicting the equilibrium properties of a body consisting of a large number of components, it is also possible for the statistical treatment to give an insight into the kinetics, i.e. the rates of change of properties, as the body

changes from one state to another. This latter subject, although important, is still in the process of development and is beyond the scope of the present work.

## 1.2. *Description of the assemblies—phase space*

Those bodies which can be treated by the methods of statistical physics will generally be composed of a large number of independent, or almost independent, components. In many cases these components will be individual particles such as electrons or photons or, in the case of a gas, individual atoms or molecules. However, in some cases, the components may be quite complex systems and, as will be seen, it is useful for certain applications to consider complete assemblies of particles as themselves forming the components of a larger physical body.

In order that the discussion given here shall be as general as possible, and also to follow common usage in this subject, the individual components of any physical body will be referred to as *systems*. The physical body in question will then be considered as an *assembly* of these systems, which may themselves be complex.

In the introductory chapters only those assemblies which consist of structureless (i.e. single particle), non-interacting systems will be considered while the more general case of systems which have an internal structure and which may be subject to interactions with other systems will be treated in the later chapters.

The state of an assembly at a given instant of time may be defined by specifying the position and either the momentum or velocity of each of the component systems. (It will be seen later that, mathematically, the definition in terms of the momentum is most convenient.) The position and momentum may be specified in cartesian coordinates by taking the position as $(x, y, z)$ in Euclidean space while the corresponding components of the momentum $(p_x, p_y, p_z)$ specify the 'position' of the system in momentum space. The state of a system is thus precisely defined by the six coordinates $x, y, z$, $p_x, p_y, p_z$, and it is, therefore, convenient to consider the system to be moving in a six-dimensional space which is termed phase space or $\Gamma$-space.*

* If the position of a system is specified by the spherical polar coordinates $(r, \theta, \phi)$, then the corresponding, or conjugate, components of momentum are $(p_r, p_\theta, p_\phi)$ where $p_r = m\,dr/dt$, $p_\theta = mr^2\,d\theta/dt$ and $p_\phi = mr^2 \sin^2\theta\, d\phi/dt$ and $m$ is the mass of the system. The corresponding phase space or $\Gamma$-space is then defined by the six coordinates $(r, \theta, \phi, p_r, p_\theta, p_\phi)$.

As it is convenient to define an element of volume in Euclidean space so that a system with coordinates in the range $x$ to $x+dx$, $y$ to $y+dy$ and $z$ to $z+dz$ lies within the volume

$$dV = dxdydz$$

it is also convenient to define an element of volume in phase space so that a system with its position and momentum coordinates in the range $x$ to $x+dx$, $y$ to $y+dy$, $z$ to $z+dz$, $p_x$ to $p_x+dp_x$, $p_y$ to $p_y+dp_y$, $p_z$ to $p_z+dp_z$ lies within a volume

$$d\Gamma = dxdydzdp_xdp_ydp_z \tag{1.1}$$

The kinetic energy of a system which has its coordinates lying within this volume $d\Gamma$ will be

$$\epsilon = \frac{p_x^2+p_y^2+p_z^2}{2m} \tag{1.2}$$

where $m$ is the mass of the system and the velocities are assumed to be non-relativistic.

As the state of a single system is defined in terms of six coordinates so it is possible to define the state of an assembly of $N$ systems in terms of $6N$ coordinates—$3N$ position coordinates and $3N$ momentum coordinates. It is sometimes convenient to allow these $6N$ coordinates to define mathematically a $6N$-dimensional phase space—a $\Gamma_{6N}$-space. The coordinates of the system $i$ may be written as $(x_i, y_i, z_i, p_{xi}, p_{yi}, p_{zi})$ and the coordinates of the assembly are then made up from all such sets with the suffix $i$ running from 1 to $N$. If the coordinates are taken to be in the range $x_i$ to $x_i+dx_i$, $p_{xi}$ to $p_{xi}+dp_{xi}$ and so on for each of the $6N$ coordinates then the 'point' representing the assembly in $\Gamma_{6N}$-space will be within the element of volume

$$\begin{aligned} d\Gamma_{6N} &= dx_1dy_1dz_1dp_{x1}dp_{y1}dp_{z1}\cdot\ldots \\ &\quad \cdot\ldots\cdot dx_idy_idz_idp_{xi}dp_{yi}dp_{zi} \\ &\quad \cdot\ldots\cdot dx_Ndy_Ndz_Ndp_{xN}dp_{yN}dp_{zN} \\ &= \prod_{i=1}^{N} dx_idy_idz_idp_{xi}dp_{yi}dp_{zi} \qquad 1.3a \\ &= \prod_{i=1}^{N} (d\Gamma)_i \qquad 1.3b \end{aligned}$$

where $(d\Gamma)_i$ is the volume element of the six-dimensional phase space for the $i$th system.

The kinetic energy of an assembly which has its coordinates within the volume $d\Gamma_{6N}$ will be given by

$$\begin{aligned} E &= \epsilon_1 + \epsilon_2 + \ldots + \epsilon_i + \ldots \epsilon_N \\ &= \sum_{i=1}^{N} \epsilon_i \\ &= \sum_{i=1}^{N} \frac{p_{xi}^2 + p_{yi}^2 + p_{zi}^2}{2m} \end{aligned} \qquad \textbf{1.4}$$

It will be seen in the subsequent discussion that a definition of the state of an assembly rather less detailed than that given above can lead to useful statistical results. However, even in this less detailed representation, it will be found useful to express the results in terms of the phase space coordinates.

## 1.3. *The average properties of an assembly*

Consider an assembly of $N$ systems which has a total energy $E$ and is contained in a volume $V$. As the state of the assembly is defined by the values of the $6N$ coordinates, the manner in which the state of the assembly is changing with time will be described by the motion of the point representing these $6N$ coordinates in $\Gamma_{6N}$-space. Although the illustration of such a motion can only be given in two dimensions, an attempt is made in Fig. 1 to indicate the changing state of an assembly. In this figure $\mathbf{p}(N)$ is taken to represent the momentum coordinates and $\mathbf{x}(N)$ to represent the position coordinates.

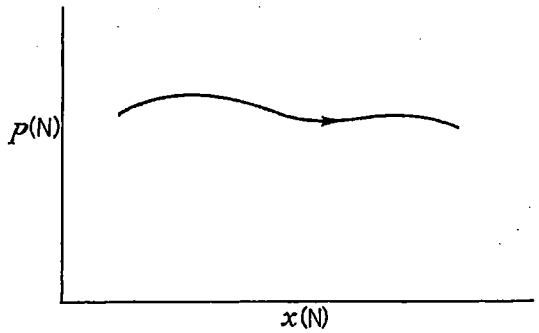


Fig. 1. Motion of a point in $\Gamma_{6N}$-space, the arrow indicating the increase of time.

If the properties of an assembly are known as functions of the position $\mathbf{x}(N)$, $\mathbf{p}(N)$ in $\Gamma_{6N}$-space (i.e. of the $6N$ coordinates of the

systems) then the average properties of the assembly will be found by averaging the known functions over all allowed positions $\mathbf{x}(N), \mathbf{p}(N)$. Reference is here made to allowed positions because, even in the absence of other restrictions, all the spatial coordinates $\mathbf{x}(N)$ will necessarily correspond to systems inside the volume $V$ of the assembly and the momentum coordinates must satisfy the equation 1.4 for the total energy of the assembly.

Consider some property $X$ of an assembly which can be written as a function of the $6N$ coordinates, i.e. as $X(\mathbf{x}(N), \mathbf{p}(N))$. If the probability that the point representing the assembly lies in the element of volume $d\Gamma_{6N}$ at $(\mathbf{x}(N), \mathbf{p}(N))$ is $P(\mathbf{x}(N), \mathbf{p}(N))\, d\Gamma_{6N}$ then the average of this property, $\overline{X}$, will be given by the normal statistical value

$$\overline{X} = \int_{\Gamma_{6N}} X(\mathbf{x}(N), \mathbf{p}(N)) P(\mathbf{x}(N), \mathbf{p}(N))\, d\Gamma_{6N} \qquad 1.5a$$

or, if the total probability has not been normalized to unity over the whole of the space $\Gamma_{6N}$,

$$\overline{X} = \frac{\int_{\Gamma_{6N}} X(\mathbf{x}(N), \mathbf{p}(N)) P(\mathbf{x}(N), \mathbf{p}(N))\, d\Gamma_{6N}}{\int_{\Gamma_{6N}} P(\mathbf{x}(N), \mathbf{p}(N))\, d\Gamma_{6N}} \qquad 1.5b$$

These averages may also be taken as a summation over all states of the assembly. If the property has a value of $X_i$ when the assembly is in the state $i$ and the probability that the assembly is in the state $i$ is $p_i$, then the average value of $X$ will be

$$\overline{X} = \frac{\sum_i p_i X_i}{\sum_i p_i} \qquad 1.6a$$

or, if the probabilities are normalized so that $\sum_i p_i = 1$,

$$\overline{X} = \sum_i p_i X_i \qquad 1.6b$$

where the summation is over all the possible states.

It will be seen in the following chapters, and in Appendix 3, that the probability function $P(\mathbf{x}(N), \mathbf{p}(N))$ may have different forms for different types of assembly. There will also be seen to be more than one method of determining the form of this probability function.

## 1.4. *Classical and quantum assemblies*

From the point of view of statistical physics the results obtained for the properties of an assembly will depend on whether the component systems are considered to obey classical or quantum mechanics. The differences in the results will arise from the fundamental differences in the assumptions which are made regarding the behaviour of the different types of systems.

If the systems in an assembly obey classical mechanics then a limitation will be imposed on the energies of the systems only if there is a definite total energy for the assembly. Also each of these classical systems will be completely distinguishable from every other system in the assembly even if the systems all belong to the same species of particle.

If, on the other hand, the systems in the assembly obey quantum mechanics, there will only be certain discrete energy levels which are available to the systems rather than the continuum of energies which are available to the classical systems. Thus, for example, in the case of the simple harmonic oscillator the only values of energy which the oscillator can take are given by $(n+\frac{1}{2})h\nu$ where $n$ is an integer, $h$ is Planck's constant and $\nu$ is the oscillator frequency. Also, unless they are considered to be localized in space as in the case of atoms at particular sites in a crystal lattice, two identical quantum mechanical systems must be taken as being completely indistinguishable.

There are two types of quantum mechanical system. If a system has an angular momentum which is half-integral in units of $h/2\pi$ or, which is equivalent, has an antisymmetric wave function, then it will obey the Pauli exclusion principle. Such a system (e.g. an electron or proton) is known as a *fermion* and will be restricted in its occupation of energy states in that no single state can be occupied by more than one such system. On the other hand, a system which has an integral value of angular momentum, and hence a symmetric wave function, will not obey the Pauli exclusion principle. This type of system (e.g. a photon or an alpha-particle) is known as a *boson* and there is no restriction on the number of such systems which may occupy a given energy state.

Because of the difference in the fundamental properties of the two types of quantum mechanical system, the fermion and the boson, it follows that the form of quantum statistics which applies to a given quantum mechanical assembly will depend on the particular nature of the component systems.

While the above discussion indicates that there will be three types of statistics, one classical and two quantum mechanical, in practice the classical case will only exist as an approximation to one of the two quantum cases since all systems will strictly obey quantum mechanics. However, there are many cases where classical statistics will give a good description of the assembly under consideration, especially where the systems are localized in space, and it is therefore convenient to commence the study of statistical physics by considering the properties of a classical assembly.

Chapter 2

# Maxwell–Boltzmann Statistics

In order that a consistent picture may be presented for the different types of statistics, the concept of energy states has been introduced even in the case of classical statistics. This approach can be justified either by considering the classical case as representing the limit where the separation of the energy levels goes to zero or by noting that the classical statistics are, strictly, only a limiting case of one of the types of quantum statistics. In any case, the results obtained for the classical assemblies by this method will be seen to have the same form as those derived on the assumption of continuous energy levels.

The statistical distribution which is now derived by determining the most probable state of a given classical assembly of non-interacting systems forms the basis of the classical or Maxwell–Boltzmann statistics.

## 2.1. *Distribution over energies*

As mentioned in the introduction it is possible to describe the state of an assembly at a given instant of time by specifying the position and momentum of each system in the assembly. However, where the systems are non-interacting, it is more useful for the purpose of the statistical analysis to specify the distribution of the systems over the various energies which are available. The detailed distribution may be given by specifying the exact energy of each of the $N$ systems of the assembly as, for example,

system 1 with energy $\epsilon_1$

system 2 with energy $\epsilon_2$

$\vdots$ $\quad$ $\vdots$

system $i$ with energy $\epsilon_i$

$\vdots$ $\quad$ $\vdots$

system $N$ with energy $\epsilon_N$

The energies of the systems will then be related to the total energy by the condition $\sum_i \epsilon_i = E$.

Alternatively, a less detailed distribution may be given by specifying the number of systems which have energies in a range $\epsilon$ to $\epsilon + d\epsilon$. This latter type of distribution is obviously more suitable for the purpose of statistical calculations and will still give all the information required about the state of the assembly.

Consider that the energies of the systems can be divided into '*sheets*' so that the sheet $s$ will include all the energy states in the range $\epsilon_s$ to $\epsilon_s + d\epsilon_s$ and the effective energy of a system in that sheet is $\epsilon_s$. The number of energy states available to the systems in the sheet $s$, $g_s$, is called the *weight* of the sheet.* The distribution of the systems over the various energies is then given by specifying the *occupation number* $n_s$ for the number of systems with energy $\epsilon_s$ in the sheet $s$. If the energies of the systems are spread over a total of $r$ energy sheets then the distribution may be written in terms of the occupation numbers as follows:

| | | | |
|---|---|---|---|
| Sheet number | 1 | 2 | 3 ... $s$ ... $r$ |
| Sheet energy | $\epsilon_1$ | $\epsilon_2$ | $\epsilon_3 \ldots \epsilon_s \ldots \epsilon_r$ |
| Weight of sheet | $g_1$ | $g_2$ | $g_3 \cdots g_s \cdots g_r$ |
| Occupation number | $n_1$ | $n_2$ | $n_3 \ldots n_s \ldots n_r$ |

where the total of the occupation numbers, $\sum_{s=1}^{r} n_s$, is equal to the total number of systems, $N$. The energy of the systems in the sheet $s$ is $n_s\epsilon_s$ and the total energy of the assembly is $\sum_{s=1}^{r} n_s\epsilon_s$.

This schematic distribution will represent one of the possible *configurations* of the assembly and each configuration of the assembly will correspond to a number of different arrangements of the systems among the energy sheets.† Thus, in a given configuration,

* By analogy with the degeneracy of an energy state in quantum mechanics $g_s$ may also be referred to as the degeneracy of the sheet $s$.

† The overall configuration of the assembly for which only the numbers of systems in an energy sheet are specified is sometimes referred to as a *macrostate*. The particular arrangements of the assembly, in which the actual system occupying a given energy state is specified, are then known as *microstates*. There will generally be a large number of microstates corresponding to a given macrostate and this number is known as the *weight* of the macrostate.

it is evidently possible to exchange two systems between two sheets and obtain a different arrangement of the systems while maintaining the same overall configuration. Similarly, a new arrangement may be produced by transferring a system from a given energy state within a sheet to another state within the same sheet although this transfer again does not produce a new configuration.

Some of the different types of arrangement which correspond to the same configuration are illustrated in Fig. 2. Here four systems, labelled *a*, *b*, *c* and *d*, are shown distributed over two energy sheets of weight $g = 3$ and $g = 4$ respectively.

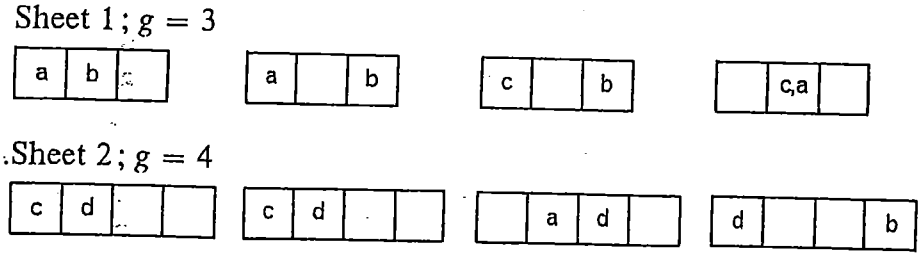


Fig. 2. Four systems *a*, *b*, *c*, *d* distributed over two sheets with two systems in sheet 1 and two systems in sheet 2. The sheets have weights 3 and 4 respectively. Calculation will show that, in the classical case where the systems are completely distinguishable, there are 864 possible arrangements corresponding to the given configuration only 4 of which are shown here.

It is necessary to note, however, that those new arrangements which are produced by interchanging two systems are only counted when the systems are classically distinguishable. When the systems are taken to be identical, as is the case in quantum statistics, it will be seen that the interchange of two such systems does not produce a new arrangement.

At this point it is necessary to introduce one of the fundamental assumptions of statistical physics, namely that

*the probability that an assembly is in a particular, allowed arrangement is the same for all such arrangements.*

(This assumption may be seen to be equivalent to a statement involving the $6N$-dimensional phase space. Thus, if the state of the assembly is represented by a point in $\Gamma_{6N}$-space, the probability that this point is within a given volume of $\Gamma_{6N}$-space is the same for all equal volumes.) The condition implied by the term *allowed*

*arrangements* arises from the conditions which may be imposed on the assembly, e.g. fixed volume and fixed energy. The justification of this assumption, however reasonable it may appear, will clearly lie in the results which are obtained from its application.

While all arrangements of the systems are assumed to be equally probable, all configurations are not. Thus a configuration in which all the $N$ systems of an assembly are in the same energy state can be produced in only one way. On the other hand, a configuration in which the $N$ systems are only specified as being distributed among the $g$ states of a particular sheet will have $g^N$ different arrangements since each system may be positioned in the sheet in $g$ different ways. A comparison of these two configurations will show that, on the basis of equal probabilities for each arrangement, the latter configuration is $g^N$ times more probable than the former.

## 2.2. *Weights of configurations*

Because the possible configurations of an assembly are not equally probable it is necessary to define a weight, $W$, for each configuration. This weight is taken as the number of distinct arrangements of the systems which all correspond to the particular configuration. The probability that an assembly is in the given configuration will then be proportional to the weight of that configuration.

If the systems in the assembly are distributed so that there are $n_s$ systems in the sheet $s$, as discussed in the previous section, the weight of this configuration will be found from the number of ways of producing the configuration with the $N$ systems of the assembly. Taking the sheets in order, the number of ways of choosing the $n_1$ systems of the first energy sheet from a total of $N$ systems is simply

$$ {}_NC_{n_1} = \frac{N!}{n_1!\,(N-n_1)!} \qquad 2.1 $$

The $n_2$ systems of the second sheet may then be chosen from the remaining $(N-n_1)$ systems in

$$ {}_{(N-n_1)}C_{n_2} = \frac{(N-n_1)!}{n_2!\,(N-n_1-n_2)!} \qquad 2.2 $$

ways. The total number of ways of choosing the systems for the

first and second sheets is then the product of the numbers in equations 2.1 and 2.2, i.e.

$$\frac{N!}{n_1!\,(N-n_1)!}\times\frac{(N-n_1)!}{n_2!\,(N-n_1-n_2)!}$$

$$=\frac{N!}{n_1!\,n_2!\,(N-n_1-n_2)!} \qquad 2.3$$

If there were only three sheets the number of systems in the third sheet would be

$$n_3 = (N-n_1-n_2)$$

and, since the choosing of the $n_1$ and $n_2$ systems will necessarily choose also the $n_3$ systems in the third sheet, the total number of ways of choosing the configuration with the numbers $n_1$, $n_2$ and $n_3$ is, from equation 2.3,

$$\frac{N!}{n_1!\,n_2!\,n_3!} \qquad 2.4$$

An extension of this argument to the case of $r$ sheets gives the number of ways of choosing the systems for the various sheets as

$$\frac{N!}{n_1!\,n_2!\,n_3!\ldots n_s!\ldots n_r!}\ * \qquad 2.5$$

Now, in the energy sheet $s$ there are $g_s$ energy states. Thus, without altering the configuration, each of the $n_s$ systems in this sheet may be placed in $g_s$ ways and there will be a total of $g_s^{n_s}$ ways of arranging the $n_s$ systems within the sheet. The total number of

* The same result may be obtained by considering the $N$ systems arranged in a line with markers placed at intervals to divide them into groups $n_1, n_2 \ldots n_s$, etc., i.e.

$$n_1\,;\ n_2\,;\ n_3\,;\ldots\,;\ n_s\,;\ldots\,;\ n_r$$

There will be $N!$ ways of arranging the systems in the line. However, this number of arrangements includes the $n_1!$ arrangements of the $n_1$ systems of sheet 1 among themselves and similarly for $n_2!, n_3!, \ldots$, etc. The total number of ways of choosing the occupation numbers $n_1, n_2, \ldots$, etc., is thus

$$\frac{N!}{n_1!\,n_2!\,n_3!\ldots n_s!\ldots n_r!}$$

This is known as the multinomial theorem.

arrangements of the systems in the given configuration, the weight of the configuration, is thus

$$W = \frac{N!}{n_1!\, n_2! \ldots n_s! \ldots n_r!} g_1^{n_1} g_2^{n_2} \ldots g_s^{n_s} \ldots g_r^{n_r} \qquad 2.6$$

Using the product symbolism $\prod_s \{g_s^{n_s}/n_s!\}$ to denote the product of the quantities $g_s^{n_s}/n_s!$ for all values of $s$ from 1 to $r$ this result becomes, more concisely,

$$\boxed{W = N! \prod_s \left\{\frac{g_s^{n_s}}{n_s!}\right\}} \qquad 2.7$$

(The type of distribution of the systems considered here has apparently ignored any possible variation of the positions of the systems over the volume of the assembly. While the effect of this positional variation will be discussed later, particularly with reference to interacting systems, it is sufficient to note here that new arrangements formed by changing the positions of non-interacting systems are allowed for in the values of the weights of the sheets, $g_s$.)

## 2.3. *The most probable configuration*

From the form of equation 2.7 it should be clear that there will be some particular values of the occupation numbers for which the weight of the corresponding configuration will be a maximum. Then, since the probability that the assembly is in a given configuration is directly proportional to the weight $W$, it follows that this configuration with the maximum weight will be the most probable configuration for the assembly.

It will be shown below that, because the assemblies under consideration are composed of very large numbers of systems, the peak of the weight $W$ in the neighbourhood of its maximum value, $W_{max}$, is extremely sharp. It follows that the assembly will spend by far the greater proportion of its time in configurations very close to the most probable one and that the average properties of the assembly will therefore correspond very closely to its properties when it is in this most probable configuration.

To find the occupation numbers which correspond to the most probable configuration it is necessary to 'maximize' the weight

$W$ by the condition

$$dW = \sum_s \frac{\partial W}{\partial n_s} dn_s = 0 \qquad 2.8$$

where the partial differentials are taken to indicate that, in each differentiation, all but one of the occupation numbers is considered constant. The solution of equation 2.8 must take into account the limitations imposed on the values of $n_s$ and $dn_s$ by the conditions that the total energy $E$, and the total number of systems, $N$, are fixed. Let the condition for a constant number of systems be expressed by the equation

$$\sum_s n_s = N = \text{constant} \qquad 2.9a$$

or

$$\sum_s dn_s = dN = 0 \qquad 2.9b$$

and the condition for a constant total energy by

$$\sum_s n_s \epsilon_s = E = \text{constant} \qquad 2.10a$$

or

$$\sum_s \epsilon_s \, dn_s = dE = 0 \qquad 2.10b$$

where the summations are taken over the values $s = 1$ to $s = r$.

The simplest method of introducing these conditions into equation 2.8 is by means of Lagrange undetermined multipliers by which the equation for a maximum in $W$ becomes

$$dW + a\,dN + b\,dE = 0 \qquad 2.11$$

where $a$ and $b$ are multipliers which are to be determined later. The justification for the introduction of the multipliers $a$ and $b$ is given briefly in Appendix 1. Substituting from equations 2.8, 2.9$b$ and 2.10$b$ in equation 2.11 gives

$$\sum_s \frac{\partial W}{\partial n_s} dn_s + a \sum_s dn_s + b \sum_s \epsilon_s \, dn_s = 0 \qquad 2.12$$

Because of the form given for $W$ by equation 2.7 it is found to be convenient to maximize $\log W$ rather than $W$ and to rewrite the equations 2.11 and 2.12 in the form*

$$d \log W + \alpha\,dN + \beta\,dE = 0 \qquad 2.13$$

* All logarithms are, of course, to be taken as natural logarithms.

and

$$\sum_s \frac{\partial \log W}{\partial n_s} dn_s + \alpha \sum_s dn_s + \beta \sum_s \epsilon_s dn_s = 0 \qquad 2.14$$

where the terms $\alpha$ and $\beta$ replace the multipliers $a$ and $b$ of equations 2.11 and 2.12. The equation 2.14 may be rewritten with the summation taken over all three terms so that

$$\sum_s \left\{ \frac{\partial \log W}{\partial n_s} + \alpha + \beta \epsilon_s \right\} dn_s = 0 \qquad 2.15$$

If $W$, and therefore $\log W$, is to be a maximum (or possibly a minimum), equation 2.15 must hold irrespective of the magnitudes of the individual increments $dn_s$. Therefore, for all values of $s$, the bracketed term in equation 2.15 must be zero and

$$\boxed{\frac{\partial \log W}{\partial n_s} + \alpha + \beta \epsilon_s = 0} \qquad 2.16$$

The differential $\partial \log W / \partial n_s$ may be evaluated with the aid of Stirling's approximation for the factorials of large numbers. The form of this approximation is discussed in Appendix 2 where it is shown that, for large numbers,

$$\log N! \simeq N \log N - N \qquad 2.17$$

Because the systems are considered to be distributed over energy sheets rather than individual energy states, the occupation numbers $n_s$ may be assumed to be sufficiently large for the approximation of equation 2.17 to apply to the case of $n_s!$ for all values of $s$.

From the value of $W$ given by equation 2.7 we derive

$$\begin{aligned} \log W &= \log N! + \log \left[ \prod_s \left\{ \frac{g_s^{n_s}}{n_s!} \right\} \right] \\ &= \log N! + \sum_s \log \left\{ \frac{g_s^{n_s}}{n_s!} \right\} \\ &\simeq N \log N - N \\ &\quad + \sum_s (n_s \log g_s - n_s \log n_s + n_s) \end{aligned} \qquad 2.18$$

Partial differentiation then gives

$$\begin{aligned} \frac{\partial \log W}{\partial n_s} &= \log g_s - \log n_s \\ &= \log \frac{g_s}{n_s} \end{aligned} \qquad 2.19$$

On substituting from equation 2.19, equation 2.16 becomes

$$\log \frac{g_s}{n_s} + \alpha + \beta\epsilon_s = 0$$

from which is obtained

$$\boxed{n_s = g_s e^{\alpha+\beta\epsilon_s}} \qquad 2.20$$

The result obtained in equation 2.20 gives the distribution of the systems over the various energy sheets for the most probable configuration and is known as the *Maxwell–Boltzmann distribution.* The term $e^{\beta\epsilon_s}$ which occurs in this distribution is often referred to as the *Boltzmann factor.* (A result of the same form as equation 2.20 is obtained in equation 10.37 but from a rather different viewpoint.)

If, instead of energy sheets, only the individual energy states are considered then a mean occupation number $\bar{n}_i$ may be defined for the state $i$ of energy $\epsilon_i$. Since such a state has a weight of unity, equation 2.20 predicts a value for this mean occupation number of

$$\bar{n}_i = e^{\alpha+\beta\epsilon_i} \qquad 2.21$$

which may, of course, be fractional.

Before the distribution given by equation 2.20 is fully defined it is obviously necessary to determine the multipliers $\alpha$ and $\beta$. It is also necessary to show that equation 2.20 does define a maximum of $W$ and that the sharpness of this maximum is sufficient to justify taking this distribution as representing the average distribution for the assembly. This question of the maximum of $W$ will be considered first.

## 2.4. *The sharpness of the configuration maximum*

The values of the occupation numbers given in equation 2.20 define a stationary point for the weight $W$. The properties of $W$ in the neighbourhood of this stationary point may be considered most conveniently by expanding the value of $\log W$ as a Taylor series about this point. This expansion will have the form

$$\log W = \log W_{\max} + \sum_s \left\{\frac{\partial \log W}{\partial n_s}\right\}_{\max} \Delta n_s + \sum_s \left\{\frac{\partial^2 \log W}{\partial n_s^2}\right\}_{\max} \frac{\Delta n_s^2}{2} + \cdots \qquad 2.22$$

where $W_{max}$ is taken as the stationary value and $W$ is the weight of the configuration for which the occupation numbers differ by $\Delta n_s$ etc. from those for $W_{max}$ (There would be additional terms in equation 2.22 of the form $\sum_s \sum_t \{\partial^2 \log W/\partial n_s \partial n_t\}_{max} \Delta n_s \Delta n_t$ besides higher order terms but since $\partial \log W/\partial n_s$ is a function of $n_s$ only, as shown by equation 2.19, these terms will be identically zero.)

Now, by definition, $\sum_s \{\partial \log W/\partial n_s\} \Delta n_s$ is zero at a stationary point of $W$. It is therefore necessary to evaluate the second order term only. From equation 2.19 $\partial \log W/\partial n_s = \log\{g_s/n_s\}$ so that

$$\frac{\partial^2 \log W}{\partial n_s^2} = -\frac{1}{n_s} \qquad 2.23$$

Writing $n_{sm}$ for the value of $n_s$ at the stationary point, substitution from equation 2.23 into equation 2.22 gives

$$\log W = \log W_{max} - \tfrac{1}{2} \sum_s \frac{\Delta n_s^2}{n_{sm}} \qquad 2.24$$

or

$$W = W_{max} \exp\left(-\tfrac{1}{2} \sum_s \frac{\Delta n_s^2}{n_{sm}}\right) \qquad 2.25$$

That the quantity $W_{max}$ is indeed the maximum value of $W$ is seen from equation 2.25 since any deviation $\Delta n_s$, positive or negative, of $n_s$ from the value $n_{sm}$ will produce a weight $W$ less than $W_{max}$.

To appreciate the sharpness of this maximum let $\Delta n_s/n_{sm} = \delta_s$ so that equation 2.25 becomes

$$W = W_{max} \exp\left(-\tfrac{1}{2} \sum_s n_{sm} \delta_s^2\right) \qquad 2.26$$

Then, if that case is considered in which all the fractional deviations have the same magnitude $|\delta_s| = \delta$ but with the signs chosen to give $\sum_s n_s \delta_s = 0$, equation 2.26 gives

$$W = W_{max} \exp\left(-\tfrac{1}{2}\delta^2 \sum_s n_{sm}\right) = W_{max} \exp(-\tfrac{1}{2} N \delta^2) \qquad 2.27$$

The average assembly considered will have a total number of systems $N$ greater than $10^{20}$ so that, even with a fractional deviation $\delta$ from the most probable configuration of one part in $10^8$ (i.e. $\delta = 10^{-8}$), the weight of the configuration will have fallen to

$$W \simeq W_{max} \exp(-\tfrac{1}{2} 10^{20} . 10^{-16}) \simeq W_{max} . 10^{-2150}$$

The rapid decrease of $W$ for values of the fractional deviation of the order of one part in $10^{10}$ is indicated in Fig. 3 for $N = 10^{20}$.

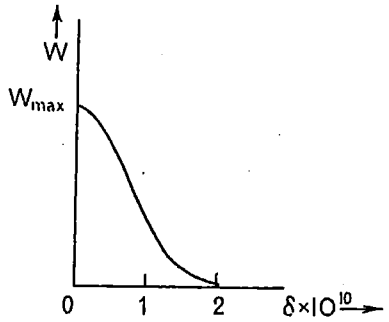


Fig. 3. Rapid decrease of $W$ with very small deviations from the most probable distribution.

It is clear from these calculations that the maximum of $W$ is extremely sharp and that only those configurations which are very close to the most probable configuration will have a probability of occurrence appreciably different from zero. It will therefore introduce no detectable error if it is assumed that the most probable configuration of the assembly is the same as its equilibrium configuration and that the properties calculated for this most probable configuration will correspond to the average properties of the assembly. (It should be clear, however, that if the number of systems in the assembly is substantially reduced, the sharpness of the configuration maximum will become less marked and fluctuations from the most probable configuration will become important.)

## 2.5. *The multiplier* $\beta$

There are a number of criteria which can be applied in considering the identity of the multiplier $\beta$. Clearly, since the number of systems having an infinite energy must be zero, equation 2.20 predicts that the value of $\beta$ is negative. Also, the value of $\beta$ may be determined by substituting in equation 2.20 for the original conditions that $\sum_s n_s = N$ and $\sum_s n_s \epsilon_s = E$. However, before proceeding with these substitutions, it is interesting to consider $\beta$ from the point of view of thermodynamics and this will now be done in two ways.

(*a*) Consider two assemblies $A'$ and $A''$ which contain $N'$ and $N''$ systems respectively. Let these assemblies be placed in 'thermal'

contact so that energy, but not systems, may be exchanged between them and let them be otherwise isolated from their surroundings. By the exchange of energy the two assemblies will eventually attain the same temperature as they come into thermal equilibrium.* The total energy $E$ of the two assemblies is now a fixed quantity and the conditions

$$dN' = 0, \qquad dN'' = 0 \qquad \text{and} \qquad dE = 0 \tag{2.28}$$

are imposed on the assemblies.

Let the energies in the two assemblies be divided into sheets and let the sheet $s$ have energies $\epsilon'_s$ and $\epsilon''_s$ and occupation numbers $n'_s$ and $n''_s$ for the assemblies $A'$ and $A''$ respectively. Then the total energy will be

$$E = \sum_s n'_s \epsilon'_s + \sum_s n''_s \epsilon''_s$$

and the conditions of equation 2.28 may be written as

$$dN' = \sum_s dn'_s = 0; \qquad dN'' = \sum_s dn''_s = 0$$

and

$$dE = \sum_s \epsilon'_s \, dn'_s + \sum_s \epsilon''_s \, dn''_s = 0 \tag{2.29}$$

If the individual weights of the two assemblies in a particular configuration are $W'$ and $W''$ respectively then the total weight of the configuration of the two assemblies taken together will be

$$W_T = W'W'' \tag{2.30}$$

each arrangement of $A'$ being taken together with every arrangement of $A''$. The condition for the most probable configuration of the combined assemblies is given, by analogy with equation 2.13, as

$$d \log W_T + \alpha' \, dN' + \alpha'' dN'' + \beta \, dE = 0 \tag{2.31}$$

where the conditions imposed by equation 2.28 are introduced through the undetermined multipliers $\alpha'$, $\alpha''$ and $\beta$. Now, from equation 2.30, $\log W_T = \log W' + \log W''$ and, since $W'$ will depend only on the occupation numbers $n'_s$,

$$d \log W' = \sum_s \frac{\partial \log W'}{\partial n'_s} dn'_s$$

and, similarly,

$$d \log W'' = \sum_s \frac{\partial \log W''}{\partial n''_s} dn''_s$$

* The 'zeroth' law of thermodynamics.

Equation 2.31 can therefore be written with the conditions taken from equation 2.29 as

$$\sum_s \frac{\partial \log W'}{\partial n'_s} dn'_s + \sum_s \frac{\partial \log W''}{\partial n''_s} dn''_s + \alpha' \sum_s dn'_s + \alpha'' \sum_s dn''_s + \beta \left( \sum_s \epsilon'_s \, dn'_s + \sum_s \epsilon''_s \, dn''_s \right) = 0$$

or

$$\sum_s \left\{ \frac{\partial \log W'}{\partial n'_s} + \alpha' + \beta \epsilon'_s \right\} dn'_s + \sum_s \left\{ \frac{\partial \log W''}{\partial n''_s} + \alpha'' + \beta \epsilon''_s \right\} dn''_s = 0 \qquad 2.32$$

Since equation 2.32 is taken as defining a stationary point it must be satisfied for any small values of $dn'_s$ and $dn''_s$ and the condition for the most probable configuration is then equivalent to the two conditions

$$\frac{\partial \log W'}{\partial n'_s} + \alpha' + \beta \epsilon'_s = 0 \qquad 2.33a$$

and

$$\frac{\partial \log W''}{\partial n''_s} + \alpha'' + \beta \epsilon''_s = 0 \qquad 2.33b$$

for all values of $s$. The equations 2.33$a$ and 2.33$b$ define the most probable distributions for the two assemblies and it is seen that both of these distributions will depend on the value of the multiplier $\beta$. Then, since it is only the temperatures of the two assemblies which necessarily have the same value, it follows that $\beta$ is a function of the temperature alone, i.e.

$$\boxed{\beta = f(T)} \qquad 2.34$$

where $T$ is the thermodynamic temperature of the assemblies. Thus, by consideration of the thermal equilibrium between two assemblies, it is possible to establish that the multiplier $\beta$ depends only on this thermodynamic temperature.

(*b*) The multiplier $\beta$ may also be considered from the point of view of its association with the change in the energy, $dE$.

Let an amount of heat $dQ$ be supplied to an assembly and let the assembly expand by an amount $dV$. The assembly will then do an amount of work $p\,dV$ where $p$ is the pressure exerted on the

assembly by its surroundings. The increase in the energy of the assembly is then given by the first law of thermodynamics as

$$dE = dQ - p\,dV \tag{2.35}$$

This change of energy will also be given by

$$dE = d\sum_s n_s\epsilon_s$$

$$= \sum_s \epsilon_s\,dn_s + \sum_s n_s\,d\epsilon_s \tag{2.36}$$

The two terms in this expression arise from the two forms of energy in equation 2.35. The change $d\epsilon_s$ of the energy level $\epsilon_s$ will be caused by a change $dV$ in the volume of the assembly* and hence the term $\sum_s n_s\,d\epsilon_s$ will be related to the work done by the assembly. The rearrangement of the systems among the energy sheets, which leads to the term $\sum_s \epsilon_s\,dn_s$, must therefore be related to the heat supplied to the assembly. A comparison between equations 2.35 and 2.36 shows therefore that the respective terms can be identified as

$$\sum_s n_s\,d\epsilon_s = -pdV \tag{2.37}$$

and

$$\sum_s \epsilon_s\,dn_s = dQ \tag{2.38}$$

(The difference between these two expressions may be considered as the difference between the 'ordered' energy or work and the 'disordered' energy or heat.)

If the result of equation 2.38 is used together with equation 2.13 for that case where there is no change in the volume of the assembly, then the equilibrium condition of the assembly becomes

$$d\log W + \alpha\,dN + \beta\,dQ = 0 \tag{2.39}$$

since any increment of energy must here be due to a supply of heat $dQ$. In the case where heat $dQ$ is supplied to an assembly with a constant number of systems (i.e. $dN = 0$) there will be a change in the weight of the assembly given by

$$d\log W = -\beta\,dQ \tag{2.40}$$

*See Appendix 5, equation A5.12.

In this expression the term $d \log W$ is a perfect differential and therefore the term $\beta\, dQ$ must be a perfect differential also. Now, it is well known in thermodynamics that the multiplier $1/T$ converts the quantity $dQ$ into the perfect differential

$$dS = \frac{dQ}{T}$$

where $S$ is the entropy of the assembly and $T$ is the temperature on the Kelvin scale. It therefore follows that, in place of the general relation given by equation 2.34, it is now possible to write

$$\boxed{\beta = -\frac{1}{kT}} \qquad 2.41$$

where $k$ is a constant and use is here made of the fact that $\beta$ must be negative. That $k$ is the well known Boltzmann constant which occurs in elementary kinetic theory will now be shown by considering the mean energy of the systems in the assembly.

(*c*) Finally, in this discussion of $\beta$, the conditions imposed on the distribution by the total energy and the number of systems in the assembly are used to determine the mean energy $\bar{\epsilon}$ of the systems. From elementary kinetic theory it is well known that this mean energy has a value derived from the ideal gas equation as

$$\bar{\epsilon} = \tfrac{3}{2}kT \qquad 2.42$$

where $k = R/N_A$ is the Boltzmann constant, $R$ being the universal gas constant and $N_A$ is Avogadro's number. Taking the energy of the assembly as $E = \sum_s n_s \epsilon_s$ and the number of systems as $N = \sum_s n_s$ gives, on substitution for $n_s$ from equation 2.20,

and
$$E = \sum_s \epsilon_s g_s e^{\alpha + \beta \epsilon_s} \qquad 2.43a$$

$$N = \sum_s g_s e^{\alpha + \beta \epsilon_s} \qquad 2.43b$$

The factor $e^{\alpha}$ may be eliminated between these two equations to give the mean energy per system as

$$\bar{\epsilon} = \frac{E}{N} = \frac{\sum_s \epsilon_s g_s e^{\beta \epsilon_s}}{\sum_s g_s e^{\beta \epsilon_s}} \qquad 2.44$$

Before this expression can be evaluated it is necessary to express $g_s$ as a function of $\epsilon_s$, the energy of the sheet, and of $d\epsilon_s$ the range of energies included in the sheet. For this purpose it is assumed that equal volumes of phase space contain equal numbers of allowed states—an assumption which is seen in Appendix 5 to be justified in the quantum mechanical case. Let there be $B$ states per unit volume of phase space so that an element $d\Gamma$ of phase space will contain $B\,d\Gamma$ states. The weight of the sheet $s$ will then be

$$g_s = B(\Delta\Gamma)_s \qquad 2.45$$

where $(\Delta\Gamma)_s$ is that volume of the six-dimensional phase space lying in the energy range $\epsilon_s$ to $\epsilon_s + d\epsilon_s$ and within the volume $V$ of the assembly.

It is shown in Appendix 4, equation A4.7, that

$$(\Delta\Gamma)_s \equiv 2\pi(2m)^{\frac{3}{2}}\epsilon_s^{\frac{1}{2}}\,d\epsilon_s\,.\,V \qquad 2.46$$

where $m$ is the mass of a component system of the assembly. (This volume of phase space is obtained by integrating the element

$$d\Gamma = dxdydzdp_xdp_ydp_z$$

over all values of $x$, $y$ and $z$ and over all directions of the momenta since the energy $\epsilon_s$ is taken to be independent of both the position of the system and its direction of motion.) Substituting from equation 2.46 in equation 2.45 gives

$$g_s \equiv BV\,.\,2\pi(2m)^{\frac{3}{2}}\epsilon_s^{\frac{1}{2}}\,d\epsilon_s \qquad 2.47$$

Substitution for $g_s$ in equation 2.44 now allows the summations over $s$ to be replaced by an integration over all the possible energies so that, on cancelling the constant terms in $g_s$ from numerator and denominator and dropping the subscript $s$,

$$\bar{\epsilon} = \frac{\int_0^\infty \epsilon^{\frac{3}{2}}e^{\beta\epsilon}\,d\epsilon}{\int_0^\infty \epsilon^{\frac{1}{2}}e^{\beta\epsilon}\,d\epsilon} \qquad 2.48$$

If it is remembered that $\beta$ is a negative quantity, partial integration of the numerator of equation 2.48 gives

$$\int_0^\infty \epsilon^{\frac{3}{2}}e^{\beta\epsilon}\,d\epsilon = -\frac{3}{2\beta}\int_0^\infty \epsilon^{\frac{1}{2}}e^{\beta\epsilon}\,d\epsilon$$

Equation 2.48 thus reduces to

$$\bar{\epsilon} = -\frac{3}{2\beta} \qquad 2.49$$

and comparison with equation 2.42 leads to the identity

$$\boxed{\beta = -\frac{1}{kT}}$$

as in equation 2.41.

## 2.6. *The multiplier* $\alpha$

In determining the multiplier $\alpha$ it is convenient to make the substitution

$$A = e^{\alpha} \qquad 2.50$$

The distribution of equation 2.20 then becomes

$$n_s = Ag_s e^{\beta\epsilon_s} \qquad 2.51$$

so that the total number of systems is

$$N = A\sum_s g_s e^{\beta\epsilon_s} \qquad 2.52$$

and

$$A = \frac{N}{\sum_s g_s e^{\beta\epsilon_s}} \qquad 2.53$$

Taking the value of $g_s$ as given by equation 2.47 gives

$$A = \frac{N}{2\pi(2m)^{\frac{3}{2}}BV\int_0^{\infty} \epsilon^{\frac{1}{2}} e^{\beta\epsilon}\, d\epsilon} \qquad 2.54$$

where again an integration over all values of $\epsilon$ has replaced the summation over $s$. Writing $-\beta\epsilon = x$ and using equation A6.9 of Appendix 6 for the $\Gamma$-integral, the integral in the denominator of equation 2.53 becomes

$$\int_0^{\infty} \epsilon^{\frac{1}{2}} e^{\beta\epsilon}\, d\epsilon = (-\beta)^{-\frac{3}{2}} \int_0^{\infty} x^{\frac{1}{2}} e^{-x}\, dx = (-\beta)^{-\frac{3}{2}}\Gamma\left(\tfrac{3}{2}\right)$$

$$= (-\beta)^{-\frac{3}{2}}\frac{\sqrt{\pi}}{2}$$

Equation 2.54 then gives

$$A = \frac{N}{BV\left(-\frac{2\pi m}{\beta}\right)^{\frac{3}{2}}}$$

or, with $\beta = -1/kT$,

$$A = \frac{N}{BV(2\pi mkT)^{\frac{3}{2}}} \qquad 2.55$$

The multiplier $\alpha$ taken from equation 2.50 is then

$$\boxed{\alpha = \log A = \log\left[\frac{N}{BV(2\pi mkT)^{\frac{3}{2}}}\right]} \qquad 2.56$$

## 2.7. *The Maxwell–Boltzmann Distribution*

Once $\beta$ and $\alpha$ are known in terms of the parameters of the assembly it is also possible to write the distribution over energies, as given by equation 2.20, in terms of these parameters. However, for this distribution to be useful, it must be expressed as a differential distribution. For example, if $dn$ is taken as the number of systems having their coordinates in a volume $d\Gamma$ of phase space then this differential distribution may be written by replacing the number of states $g_s$ in equation 2.20 by $B\,d\Gamma$ to give

$$dn = e^{\alpha+\beta\epsilon}B\,d\Gamma \qquad 2.57$$

Alternatively, if $g(\epsilon)\,d\epsilon$ is the number of states with energies in the range $\epsilon$ to $\epsilon+d\epsilon$, equation 2.20 gives

$$n(\epsilon)\,d\epsilon = e^{\alpha+\beta\epsilon}g(\epsilon)\,d\epsilon \qquad 2.58$$

for the number of systems having energies in the range $\epsilon$ to $\epsilon+d\epsilon$. The value of $g(\epsilon)\,d\epsilon$ will be simply that given for the weight $g_s$ by equation 2.47 with $\epsilon_s$ replaced by $\epsilon$.* Thus, on substituting for $\alpha$ and $\beta$ from equations 2.56 and 2.41 respectively, equation 2.58 becomes

$$\boxed{n(\epsilon)\,d\epsilon = \frac{2\pi N}{(\pi kT)^{\frac{3}{2}}}e^{-\epsilon/kT}\epsilon^{\frac{1}{2}}\,d\epsilon} \qquad 2.59$$

* As will be mentioned later, the quantity $g(\epsilon)$ is frequently referred to as the *density of states.*

This is the Maxwell–Boltzmann distribution in differential form.

It is of interest to note here that the distribution in equation 2.59 is independent of the constant $B$. From this it may be concluded that, in the completely classical limit where the separation of energy levels disappears, the same distribution will be obtained.

## PROBLEMS

1. Show that the same distribution is obtained from equation 2.11 as from equation 2.13 independently of whether the form of Stirling's approximation is taken as $N! \cong \{N/e\}^N$ or, more accurately, as $N! \equiv \{N/e\}^N \sqrt{(2\pi N)}$.

2. By direct integration of $\int_0^\infty \epsilon n(\epsilon)\, d\epsilon$ with $n(\epsilon)$ taken from equation 2.59 show that the total energy of the assembly is $\frac{3}{2}RT$ where $R = Nk$.

Chapter 3

# Applications of Maxwell-Boltzmann Statistics

## 3.1. *Average properties of systems*

Let there be some property of a system $Y(\mathbf{x}, \mathbf{p})$ which is a function of its six coordinates represented by $\mathbf{x} \equiv x, y, z$ and $\mathbf{p} \equiv p_x, p_y, p_z$. Now that the distribution of the systems over the available energies is known it is possible to express the average value of $Y(\mathbf{x}, \mathbf{p})$ in terms of this distribution. If there are $dn$ systems with coordinates $(\mathbf{x}, \mathbf{p})$ in the element of phase space $d\Gamma = dxdydzdp_x dp_y dp_z$ then the probability of finding the system in this element of phase space can be written as

$$f(\mathbf{x}, \mathbf{p})\, d\Gamma = \frac{dn}{N} \tag{3.1}$$

where $N$ is the total number of systems and $f(\mathbf{x}, \mathbf{p})$ is a probability function. With $dn$ taken from equation 2.57 this gives

$$f(\mathbf{x}, \mathbf{p})\, d\Gamma = \frac{e^{\alpha + \beta\epsilon} B\, d\Gamma}{N} \tag{3.2}$$

The mean value of $Y(\mathbf{x}, \mathbf{p})$ is obtained by taking the normal statistical average in the form

$$\overline{Y} = \frac{\int_\Gamma Y(\mathbf{x}, \mathbf{p}) f(\mathbf{x}, \mathbf{p})\, d\Gamma}{\int_\Gamma f(\mathbf{x}, \mathbf{p})\, d\Gamma} \tag{3.3}$$

where the integral is taken over all allowed regions of phase space and it is frequently convenient to introduce the integral in the denominator even though $\int_\Gamma f(\mathbf{x}, \mathbf{p})\, d\Gamma$ is, by definition, unity. Substitution from equation 3.2 into equation 3.3 gives, on cancellation of the common terms $e^\alpha B/N$,

$$\boxed{\overline{Y} = \frac{\int_\Gamma Y(\mathbf{x}, \mathbf{p}) e^{-\epsilon/kT}\, d\Gamma}{\int_\Gamma e^{-\epsilon/kT}\, d\Gamma}} \tag{3.4}$$

where the substitution has been made for $\beta = -1/kT$.

In section 1.3 a discussion was given of the average value of some property of the assembly as a whole. Taking this property as $X(\mathbf{x}(N), \mathbf{p}(N))$, a function of the $6N$ coordinates of the systems, the average was given in equation 1.5*b* as

$$\bar{X} = \frac{\int_{\Gamma_N} X(\mathbf{x}(N), \mathbf{p}(N)) P(\mathbf{x}(N), \mathbf{p}(N))\, d\Gamma_{6N}}{\int_{\Gamma_N} P(\mathbf{x}(N), \mathbf{p}(N))\, d\Gamma_{6N}} \qquad 1.5b$$

where $P(\mathbf{x}(N), \mathbf{p}(N))\, d\Gamma_{6N}$ is the probability that the assembly has its coordinates in the element of $6N$-dimensional phase space $d\Gamma_{6N}$. The integral is taken over all allowed regions of this phase space.

The probability that the coordinates of all the systems lie in the element $d\Gamma_{6N}$ will be the product of the individual probabilities $(f(\mathbf{x}, \mathbf{p})\, d\Gamma)_i$ that the $i$th system has its coordinates in the corresponding six-dimensional element $(d\Gamma)_i$. Thus,

$$P(\mathbf{x}(N), \mathbf{p}(N))\, d\Gamma_{6N} = \prod_{i=1}^{N} (f(\mathbf{x}, \mathbf{p})\, d\Gamma)_i$$

Now, as shown in equation 1.3*b*, $\prod_{i=1}^{N} (d\Gamma)_i = d\Gamma_{6N}$ and so

$$P(\mathbf{x}(N), \mathbf{p}(N)) = \prod_{i=1}^{N} f(\mathbf{x}, \mathbf{p})_i$$

which becomes, on taking equation 3.2 in the form $(f(\mathbf{x}, \mathbf{p}))_i = (e^{\alpha} B/N)\, e^{-\epsilon_i/kT}$ where $\epsilon_i$ is the energy of system $i$,

$$P(\mathbf{x}(N), \mathbf{p}(N)) = \prod_{i=1}^{N} \frac{e^{\alpha} B}{N} e^{-\epsilon_i/kT}$$

$$= \left\{\frac{e^{\alpha} B}{N}\right\}^{N} \exp\, -\left(\sum_{i=1}^{N} \epsilon_i/kT\right)$$

Now, $\sum_{i=1}^{N} \epsilon_i = E$, the total energy of the assembly, so that

$$P(\mathbf{x}(N), \mathbf{p}(N)) = \left\{\frac{e^{\alpha} B}{N}\right\}^{N} e^{-E/kT} \qquad 3.5$$

Substitution in equation 1.5*b* now gives, on cancelling the common term $\{e^{\alpha} B/N\}^N$,

$$\bar{X} = \frac{\int_{\Gamma_{6N}} X(\mathbf{x}(N), \mathbf{p}(N))\, e^{-E/kT}\, d\Gamma_{6N}}{\int_{\Gamma_{6N}} e^{-E/kT}\, d\Gamma_{6N}} \qquad 3.6$$

The discussion of this last expression will be left until consideration is given to those assemblies for which the total energy is not a fixed quantity and interactions between the component systems are not negligible. In the present case where interactions between the systems are neglected and the energy of the assemblies is a fixed quantity equation 3.6 gives little additional useful information.

## 3.2. *The classical perfect gas*

By the definition of a classical perfect gas as an assembly of non-interacting molecules, each distinguishable from the other, it is clear that, for such a gas, the classical, Maxwell–Boltzmann statistics are applicable. It is not necessary to assume that the volume occupied by the individual molecules is negligible since this volume could easily be included in the theory by taking the integrals over phase space to be only over the volume which is actually available to the molecules. However, for convenience, the volume of the molecules will be ignored in the present discussion.

In considering the properties of a perfect gas it is useful to give the distributions of the properties of the molecules in more than one form. Already the distribution of the energies has been given in equation 2.59 where $n(\epsilon)\,d\epsilon$ was taken as the number of molecules with energies in the range $\epsilon$ to $\epsilon+d\epsilon$. If the distribution is expressed as a function of momentum or velocity then it is possible to take $n_p(p)\,dp$ as the number of molecules with momentum in the range $p$ to $p+dp$ and $n_v(v)\,dv$ as the number with velocity in the range $v$ to $v+dv$.

The element of phase space corresponding to a volume $V$ (i.e. $\int_V dxdydz = V$) and to a total momentum in the range $p$ to $p+dp$ is given in Appendix 4 (equation A4.4) as

$$\Delta\Gamma(p \to p+dp) = 4\pi p^2\,dp\,.\,V$$

The corresponding element for a total velocity in the range $v$ to $v+dv$ is obtained by substituting $p = mv$ to give (see equation A4.6)

$$\Delta\Gamma(v \to v+dv) = m^3\,.\,4\pi v^2\,dv\,.\,V$$

Substituting for these values of $\Delta\Gamma$ in equation 2.57, and putting $e^{\alpha} = N/BV(2\pi mkT)^{\frac{3}{2}}$, gives the momentum and velocity distri-

butions as

$$n_p(p)\,dp = \frac{4\pi N}{(2\pi mkT)^{\frac{3}{2}}}\, e^{-p^2/2mkT} p^2\,dp \qquad 3.7$$

and

$$n_v(v)\,dv = 4\pi N\left\{\frac{m}{2\pi kT}\right\}^{\frac{3}{2}} e^{-mv^2/2kT} v^2\,dv \qquad 3.8$$

(The left-hand sides of the equations 3.7 and 3.8 are equivalent to the number of systems, $dn$, as given in equation 2.57 for the respective volumes of phase space.)

These distributions, in which the energy has been expressed as $p^2/2m$ and $\frac{1}{2}mv^2$ respectively, can be compared with the energy distribution of equation 2.59, i.e.

$$n(\epsilon)\,d\epsilon = \frac{2\pi N}{(\pi kT)^{\frac{3}{2}}}\, e^{-\epsilon/kT} \epsilon^{\frac{1}{2}}\,d\epsilon$$

The result presented in equation 3.8 is known as the Maxwell Velocity Distribution and its form is indicated in Fig. 4 for different values of the temperature of the gas.* While, strictly speaking,

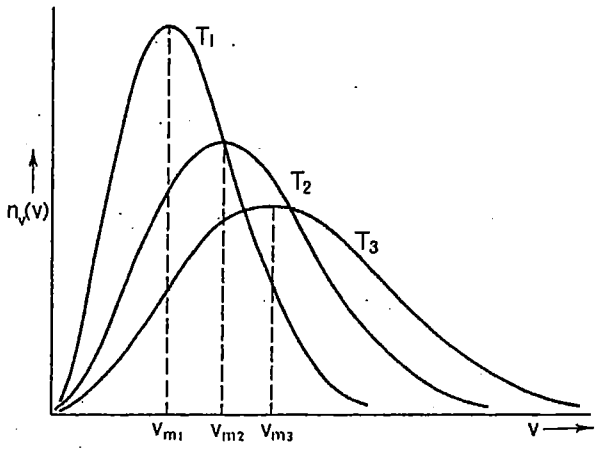


Fig. 4. The Maxwell velocity distribution for the temperatures $T_1 < T_2 < T_3$.

it is a *speed* distribution which is defined by equation 3.8 since $v$ is taken independent of direction, the expression *velocity distribution* is in general use.

* For a review of the methods by which the form of this distribution has been verified experimentally, the reader is referred to the text by Sir James Jeans: *Introduction to the Kinetic Theory of Gases*, O.U.P. pp. 129ff.

A velocity distribution for a perfect gas may also be given in terms of the three component velocities of the molecules; $v_x$, $v_y$ and $v_z$. Since $p_x = mv_x$, etc., the element of phase space for the velocity range $v_x$ to $v_x + dv_x$, $v_y$ to $v_y + dv_y$ and $v_z$ to $v_z + dv_z$ is

$$\Delta\Gamma = V.m^3\, dv_x dv_y dv_z \qquad 3.9$$

for a gas of volume $V$ (see equation A4.5). Substitution for this value of $\Delta\Gamma$ in equation 2.57 and for $e^{\alpha}$ from equation 2.55 gives the number of molecules in the element of velocity space $dv_x dv_y dv_z$ as

$$n_3(v_x, v_y, v_z)\, dv_x dv_y dv_z = N\left\{\frac{m}{2\pi kT}\right\}^{\frac{3}{2}} \times \exp[-m(v_x^2 + v_y^2 + v_z^2)/2kT] \times dv_x dv_y dv_z \qquad 3.10$$

where the energy has been written as $\frac{1}{2}m(v_x^2 + v_y^2 + v_z^2)$. Again the left-hand side of the equation represents the number $dn$ in equation 2.57 for the particular volume $\Delta\Gamma$ of phase space.

(It is left as an exercise for the student to show that the integration of equation 3.10 over all values of the polar angles $\theta$ and $\phi$, as indicated in Appendix 4 for the momentum, leads to the velocity distribution of equation 3.8.)

The number of molecules $n_x(v_x)\, dv_x$, which have a velocity component $v_x$ to $v_x + dv_x$ irrespective of the values of the other components, may be found by integrating the expression in equation 3.10 over all possible values of $v_y$ and $v_z$. Thus

$$\begin{aligned} n_x(v_x)\, dv_x &= \left\{\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} n_3(v_x, v_y, v_z)\, dv_y dv_z\right\} dv_x \\ &= N\left\{\frac{m}{2\pi kT}\right\}^{\frac{3}{2}} \left\{\int_{-\infty}^{\infty} \exp(-mv_y^2/2kT)\, dv_y \right. \\ &\quad \left. \times \int_{-\infty}^{\infty} \exp(-mv_z^2/2kT)\, dv_z\right\} \\ &\quad \times \exp(-mv_x^2/2kT)\, dv_x \end{aligned} \qquad 3.11$$

Using the value of the definite integral as given in Appendix 6 (see equation A6.12) as $\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{(\pi/a)}$, equation 3.11

becomes

$$n_x(v_x)\,dv_x = N\left\{\frac{m}{2\pi kT}\right\}^{\frac{1}{2}} \exp(-mv_x^2/2kT)\,dv_x \qquad 3.12$$

there being similar expressions for $n_y(v_y)\,dv_y$ and $n_z(v_z)\,dv_z$.

If the probability distribution function $f_x(v_x)$ is defined as $n_x(v_x)/N$ so that $f_x(v_x)\,dv_x$ is the probability that the $x$-component of the velocity is in the range $v_x$ to $v_x + dv_x$ then, from equation 3.12,

$$f_x(v_x) = \left\{\frac{m}{2\pi kT}\right\}^{\frac{1}{2}} \exp(-mv_x^2/2kT) \qquad 3.13$$

There is a corresponding probability function for the three velocities together which is obtained from equation 3.10 as

$$f_3(v_x, v_y, v_z) = \frac{n_3(v_x, v_y, v_z)}{N}$$

$$= \left\{\frac{m}{2\pi kT}\right\}^{\frac{3}{2}} \exp[-m(v_x^2 + v_y^2 + v_z^2)/2kT) \qquad 3.14$$

where $f_3(v_x, v_y, v_z)\,dv_x dv_y dv_z$ is the probability that a molecule has velocity components $v_x$ to $v_x + dv_x$, $v_y$ to $v_y + dv_y$, $v_z$ to $v_z + dv_z$. A comparison between equations 3.13 and 3.14 clearly leads to the relationship

$$f_3(v_x, v_y, v_z) = f_x(v_x) f_y(v_y) f_z(v_z) \qquad 3.15^*$$

## 3.3. *Mean and most probable velocities*

Unless the gas as a whole is undergoing a translational movement the mean *velocity* of the molecules in the gas will strictly be zero. At the same time it is possible to determine a mean speed for the

* Maxwell's original derivation of the velocity distribution was based on the assumption that equation 3.15 is true. That this assumption is only valid for non-relativistic velocities is clear if the kinetic energy in equation 3.14 is written as

$$mc^2\left\{\frac{1}{\sqrt{1 - \dfrac{(v_x^2 + v_y^2 + v_z^2)}{c^2}}} - 1\right\}$$

instead of $\frac{1}{2}m(v_x^2 + v_y^2 + v_z^2)$. It follows then that the usual proof of the Maxwell velocity distribution must not be taken as a general proof of the Maxwell–Boltzmann energy distribution.

molecules. This mean speed, or mean velocity as it is most frequently termed, may be determined either with the aid of equation 3.4 or by defining a probability function similar to those given in the previous section. Thus, if $f_v(v)\,dv$ is the probability that a molecule has a total velocity in the range $v$ to $v+dv$ then, by equation 3.8,

$$f_v(v)\,dv = \frac{n_v(v)\,dv}{N} = 4\pi\left\{\frac{m}{2\pi kT}\right\}^{\frac{3}{2}} \exp(-mv^2/2kT)v^2\,dv \qquad 3.16$$

With this probability function the mean velocity of the molecules is, by definition,

$$\bar{v} = \int_0^\infty v f_v(v)\,dv \qquad \textbf{3.17}a$$

$$= 4\pi\left\{\frac{m}{2\pi kT}\right\}^{\frac{3}{2}} \int_0^\infty \exp(-mv^2/2kT)v^3\,dv \qquad \textbf{3.17}b$$

Using the form of the Γ-integral given in equation A6.12 of Appendix 6,

$$\int_0^\infty e^{-av^2}v^3\,dv = \frac{1}{2a^2}\Gamma(2) \equiv \frac{1}{2a^2}$$

and equation 3.17*b* gives

$$\boxed{\bar{v} = \sqrt{\left(\frac{8kT}{\pi m}\right)}} \qquad 3.18$$

The value of the mean square velocity $\overline{v^2}$, may be determined in a manner similar to that used for the mean velocity. Thus

$$\overline{v^2} = \int_0^\infty v^2 f_v(v)\,dv \qquad 3.19a$$

$$= 4\pi\left\{\frac{m}{2\pi kT}\right\}^{\frac{3}{2}} \int_0^\infty \exp(-mv^2/2kT)v^4\,dv \qquad 3.19b$$

Again using equation A6.12,

$$\int_0^\infty e^{-av^2}v^4\,dv = \frac{1}{2a^{\frac{5}{2}}}\Gamma\left(\frac{5}{2}\right) = \frac{1}{2a^{\frac{5}{2}}}\cdot\frac{3}{4}\sqrt{\pi}$$

and equation 3.19*b* gives

$$\boxed{\overline{v^2} = \frac{3kT}{m}} \qquad 3.20$$

This is, of course, identical with the value obtained in simple kinetic theory by setting the mean energy $\frac{1}{2}m\overline{v^2}$ equal to $\frac{3}{2}kT$.

The most probable velocity (or speed), $v_m$, is that velocity for which the probability function $f_v(v)$ is a maximum. Taking $f_v(v)$ from equation 3.16 this maximum value occurs when

$$\frac{df_v(v)}{dv} = 4\pi\left\{\frac{m}{2\pi kT}\right\}^{\frac{3}{2}}\left\{2v - \frac{mv^3}{kT}\right\}\exp(-mv^2/2kT) = 0$$

or

$$2v_m - \frac{mv_m^3}{kT} = 0$$

That is, ignoring the minimum at $v_m = 0$,

$$\boxed{v_m = \sqrt{\left(\frac{2kT}{m}\right)}} \qquad 3.21$$

(It is left as an exercise for the student to show that $\overline{v_x^2} = kT/m = \frac{1}{3}\overline{v^2}$ and that $|\bar{v}_x| = \{kT/2\pi m\}^{\frac{1}{2}} = \frac{1}{4}\bar{v}$. Care should be taken to note that, in most cases where the cartesian components (i.e. $v_x$, etc.) are considered, the integrals must generally be taken over the range $-\infty \leqslant v_x \leqslant \infty$ whereas, in the integrals involving the total velocity $v$, the range of integration is $0 \leqslant v \leqslant \infty$.)

## 3.4. *The Doppler broadening of spectral lines*

One of the effects which arises from the distribution of the velocities of the molecules in a gas is the broadening of the spectral lines which are emitted by the gas molecules. This broadening, which is due to the Doppler effect, can be used as an experimental check for the validity of the Maxwell velocity distribution.

Consider gas molecules which are emitting radiation of normal wave-length $\lambda_0$ in the $x$-direction. Let a particular molecule be moving with a component velocity $v_x$ towards an observer as shown in Fig. 5 and let the radiation from this molecule, as received by the observer, be of wave-length $\lambda$. This wave-length will

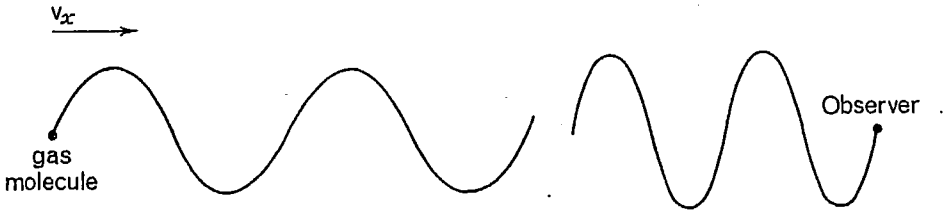


Fig. 5. Observer receiving radiation from a moving gas molecule.

be given by the normal Doppler expression, i.e.

$$\lambda = \lambda_0\left(1-\frac{v_x}{c}\right) \qquad 3.22$$

where $c$ is the velocity of light. The velocity $v_x$ may thus be written in terms of the observed wave-length $\lambda$ by rearranging equation 3.22 so that

$$v_x = \frac{c(\lambda_0-\lambda)}{\lambda_0} \qquad 3.23a$$

and

$$dv_x = -\frac{c}{\lambda_0}d\lambda \qquad 3.23b$$

Since the fraction of molecules having a component velocity in the range $v_x$ to $v_x+dv_x$ is given by equation 3.13 as

$$\left\{\frac{m}{2\pi kT}\right\}^{\frac{1}{2}} \exp(-mv_x^2/2kT)\,dv_x$$

the fraction of the radiation $f_\lambda(\lambda)\,d\lambda$ which is received by the observer in the wave-length range $\lambda$ to $\lambda+d\lambda$ is obtained by substituting for $v_x$ and $dv_x$ from the equations 3.23 so that

$$f_\lambda(\lambda)\,d\lambda = \left\{\frac{m}{2\pi kT}\right\}^{\frac{1}{2}} \exp\left\{-\frac{mc^2}{2kT}\left|\frac{\lambda_0-\lambda}{\lambda_0}\right|^2\right\}\frac{c}{\lambda_0}d\lambda \qquad 3.24$$

The negative sign of equation 3.23*b* only relates to the direction chosen for $v_x$ and does not affect the magnitude of $f_\lambda(\lambda)$. It is therefore not included in equation 3.24.

The intensity of radiation emitted in the wave-length range $\lambda$ to $\lambda+d\lambda$ will be given by equation 3.24 as

$$I(\lambda)\,d\lambda = Cf_\lambda(\lambda)\,d\lambda$$
$$= I(\lambda_0)\exp\left\{-\frac{mc^2}{2kT}\left|\frac{\lambda_0-\lambda}{\lambda_0}\right|^2\right\}d\lambda \qquad 3.25$$

where $C$ is a constant and $I(\lambda_0)$ is the intensity emitted per unit range of wave-length at $\lambda_0$. The distribution of the intensity as a function of wave-length will therefore have the form of a Gaussian curve about $\lambda_0$ as shown in Fig. 6.

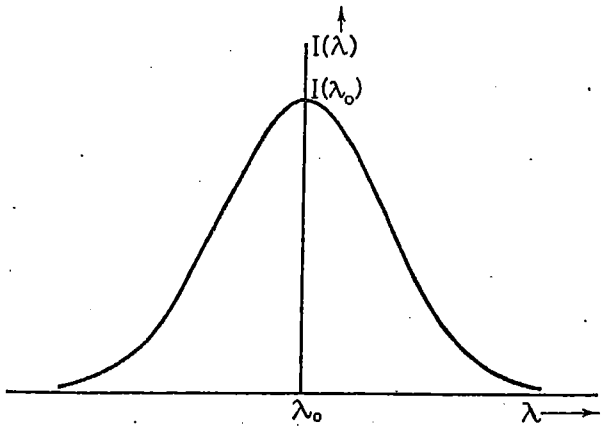


Fig. 6. Spectral intensity for a line subject to Doppler broadening.

If the spectral intensity is measured for a line which has been broadened due to the Doppler effect then, assuming equation 3.25, it is possible to determine the temperature of the emitting gas. This temperature measurement is possible both at values above those measurable by conventional techniques and also over extremely short time intervals.

## 3.5. *Equipartition of energy*

If the energy of the systems in an assembly is made up of terms quadratic in the position and momentum coordinates of the systems then, for each such quadratic term, the contribution to the mean energy will be $\frac{1}{2}kT$ where $T$ is the temperature of the assembly. This fact is illustrated by the following examples.

Consider first a gas molecule of mass $m$ and let its energy due to its motion in the $x$-direction be quadratic in the momentum $p_x$, i.e. $\epsilon_x = p_x^2/2m$. The mean value of $\epsilon_x$ is given by equation 3.4 so that, at temperature $T$,

$$\bar{\epsilon}_x = \frac{\int_\Gamma p_x^2/2m\, e^{-\epsilon/kT}\, d\Gamma}{\int_\Gamma e^{-\epsilon/kT}\, d\Gamma} \qquad 3.26$$

where the energy $\epsilon$ is the total energy including $\epsilon_x$. Taking the energy in two parts as $p_x^2/2m$ and $\{\epsilon - p_x^2/2m\}$ so that the second

term is independent of $p_x$ allows equation 3.26 to be written as

$$\bar{\epsilon}_x = \frac{\int \exp\left\{-\left(\epsilon - \frac{p_x^2}{2m}\right)/kT\right\} dx dy dz dp_y dp_z \int_{-\infty}^{\infty} \frac{p_x^2}{2m} \exp(-p_x^2/2mkT)\, dp_x}{\int \exp\left\{-\left(\epsilon - \frac{p_x^2}{2m}\right)/kT\right\} dx dy dz dp_y dp_z \int_{-\infty}^{\infty} \exp(-p_x^2/2mkT)\, dp_x} \qquad 3.27$$

with the five-fold integral taken over all allowed values of $x$, $y$, $z$, $p_y$ and $p_z$. Writing $p_x^2/2mkT = u^2$ and cancelling the five-fold integral allows equation 3.27 to be written as

$$\bar{\epsilon}_x = \frac{kT \int_{-\infty}^{\infty} e^{-u^2} u^2\, du}{\int_{-\infty}^{\infty} e^{-u^2}\, du} \qquad 3.28$$

Integration by parts gives $\int_{-\infty}^{\infty} e^{-u^2} u^2\, du = \frac{1}{2}\int_{-\infty}^{\infty} e^{-u^2}\, du$ so that equation 3.28 becomes

$$\bar{\epsilon}_x = \tfrac{1}{2}kT \qquad 3.29$$

A similar result to that of equation 3.29 would have been obtained had the energy in the $x$-direction been taken as quadratic in the coordinate $x$, i.e. $\epsilon_x = \frac{1}{2}\mu x^2$. However, if the energy is composed of more than one term, the energy may be evaluated either by splitting the integrals or in the following manner.

Consider a one-dimensional simple harmonic oscillator which has its energy composed of two quadratic terms, i.e.

$$\epsilon_x = \frac{p_x^2}{2m} + \tfrac{1}{2}\mu x^2 \qquad 3.30$$

where $\mu$ is the restoring force per unit displacement of the oscillator. The mean energy of the oscillator at temperature $T$ is again given by equation 3.4 and is

$$\overline{\epsilon_x} = \frac{\int_\Gamma \{p_x^2/2m + \frac{1}{2}\mu x^2\}\, e^{-\epsilon/kT}\, d\Gamma}{\int_\Gamma e^{-\epsilon/kT}\, d\Gamma} \qquad 3.31$$

If the common integral of $\exp\{-(\epsilon - p_x^2/2m - \frac{1}{2}\mu x^2)/kT\}\, dy dz dp_y dp_z$ taken over all values of $y$, $z$, $p_y$ and $p_z$ is cancelled from equation

3.31 the mean energy becomes

$$\bar{\epsilon}_x = \frac{\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\left\{\frac{p_x^2}{2m}+\frac{1}{2}\mu x^2\right\}\exp\left\{-\left(\frac{p_x^2}{2m}+\frac{1}{2}\mu x^2\right)/kT\right\}dx\,dp_x}{\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\exp\left\{-\left(\frac{p_x^2}{2m}+\frac{1}{2}\mu x^2\right)/kT\right\}dx\,dp_x} \qquad 3.32$$

the only restriction on the motion in the $x$-direction being imposed by the restoring force acting on the oscillator. In order to evaluate the integrals of equation 3.32 the coordinates $p_x$ and $x$ may be expressed in polar form so that

$$\frac{p_x^2}{2m} = r^2\sin^2\theta, \qquad \tfrac{1}{2}\mu x^2 = r^2\cos^2\theta$$

Then $dp_x dx \equiv 2(m/\mu)^{\frac{1}{2}} r\,dr d\theta$ and equation 3.32 then gives, on integrating over all values of $\theta$ and $r$,

$$\bar{\epsilon}_x = \frac{\int_0^{2\pi} d\theta \int_0^{\infty} e^{-r^2/kT} r^3\,dr}{\int_0^{2\pi} d\theta \int_0^{\infty} e^{-r^2/kT} r\,dr}$$

$$= kT \qquad 3.33$$

where use has been made of equation A6.12 (Appendix 6). The energy given by equation 3.33 is in agreement with the value given by $\frac{1}{2}kT$ for each quadratic term.

The mean energy of a free structureless molecule will be given, on a similar analysis, by

$$\bar{\epsilon} = \left\{\frac{p_x^2}{2m}+\frac{p_y^2}{2m}+\frac{p_z^2}{2m}\right\} = \tfrac{1}{2}kT+\tfrac{1}{2}kT+\tfrac{1}{2}kT$$

$$= \tfrac{3}{2}kT$$

in agreement with equation 2.42 while the mean energy of a three-dimensional oscillator will be

$$\bar{\epsilon} = \left\{\frac{p_x^2}{2m}+\tfrac{1}{2}\mu_1 x^2+\frac{p_y^2}{2m}+\tfrac{1}{2}\mu_2 y^2+\frac{p_z^2}{2m}+\tfrac{1}{2}\mu_3 z^2\right\}$$

$$= 6\,.\,\tfrac{1}{2}kT$$

$$= 3kT \qquad 3.34$$

It is usual, and useful, to refer to each independent quadratic term in the energy as a 'degree of freedom' of the system and then

an average energy of $\frac{1}{2}kT$ is assigned to each degree of freedom or independent mode of taking energy. As an example consider a gramme atom of a solid element containing $N_A$ atoms, where $N_A$ is Avogadro's number. If each atom is considered to behave as a three-dimensional harmonic oscillator there will be a total of $6N_A$ degrees of freedom. The energy of the gramme atom of solid at temperature $T$ will be

$$\begin{aligned} E &= 6N_A \cdot \tfrac{1}{2}kT \\ &= 3RT \end{aligned} \qquad 3.35$$

The specific heat per gramme atom of the solid element will then be

$$C_v = \left\{\frac{\partial E}{\partial T}\right\}_V = 3R \qquad 3.36$$

$$\simeq 5{\cdot}94 \text{ cal/°K/gramme atom}$$

if the volume of the solid is maintained constant. This is the result which was obtained by Dulong and Petit for the specific heat of a metal.

A further discussion of degrees of freedom is given in the following section.

## 3.6. *The specific heats of gases*

Because of the equipartition of energy, if a given molecule has $f$ degrees of freedom then, in a classical gas at temperature $T$, it will have an average energy of $(f \times \frac{1}{2}kT)$. The energy of a gramme molecule of the gas at temperature $T$ will thus be

$$E = N_A \times f \times \tfrac{1}{2}kT \qquad 3.37$$

The corresponding specific heat of the gas at constant volume is then

$$\begin{aligned} C_v &= \left\{\frac{\partial E}{\partial T}\right\}_v = \tfrac{1}{2}N_A kf \\ &= \tfrac{1}{2}Rf \end{aligned} \qquad 3.38$$

per gramme molecule.

If the gas molecules are monatomic, only the three components of the kinetic energy of translation will contribute to the energy

of the gas. There will then be three degrees of freedom, i.e. $f = 3$. (As will be discussed later, any change in the rotational motion of the atom about an axis through its centre will require an energy so large compared with the normal thermal energy $kT$ that such rotation is said to be 'hindered'.) The specific heat of the gas is obtained from equation 3.38, with $f = 3$, as

$$C_v \text{ (monatomic)} = \tfrac{3}{2}R \qquad 3.39$$

If the molecules of the gas are diatomic there will be five degrees of freedom. Besides the three degrees of freedom of translation which were present for the monatomic molecules there will be two degrees of freedom of rotation as illustrated in Fig. 7. If the axis

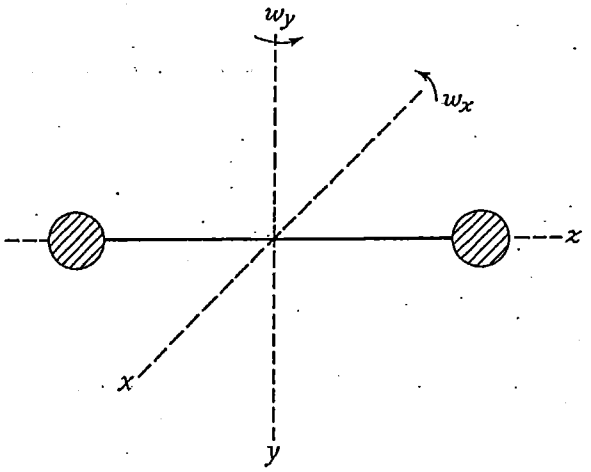


Fig. 7. Possible rotations of a diatomic molecule.

joining the two atoms of the molecule is taken as the $z$-axis the rotational energy is given by two quadratic terms as

$$E_{\text{rot}} = \tfrac{1}{2}I_x\omega_x^2 + \tfrac{1}{2}I_y\omega_y^2$$

where $I_x$ and $I_y$ are the moments of inertia about the $x$- and $y$-axes and $\omega_x$, $\omega_y$ are the appropriate angular velocities. The rotation of the molecule about its own axis is again hindered at normal temperatures and this is also the case, in general, with the vibration of the atoms along their axis. The specific heat is obtained by substituting for $f = 5$ in equation 3.38 to give

$$C_v \text{ (diatomic)} = \tfrac{5}{2}R \qquad 3.40$$

For a triatomic, or more complex, molecule there are generally six degrees of freedom. Of these there are three degrees of freedom

of translation together with three degrees of freedom of rotation corresponding to three independent axes about which the rotation is not hindered at normal temperatures. Substituting for $f = 6$ in equation 3.38 gives the specific heat for such gases as

$$C_v\,(\text{triatomic}) = 3R \qquad 3.41$$

While this value may hold for some types of molecules with more than two atoms, in many cases there are contributions from vibrational energy and the value of $f$ will be greater than six. A fuller discussion of this point must be left, however, until section 8.3 on the diatomic molecule.

If use is made of the relationship between the principal specific heats of a perfect gas, namely that

$$C_p - C_v = R$$

then the ratio $\gamma = C_p/C_v$ may be determined for each of the three cases considered here. If the value of $C_v$ is taken from equation 3.38 as $\frac{1}{2}Rf$ then $C_p = R(1+\frac{1}{2}f)$ and

$$\gamma = 1 + \frac{2}{f}$$

Then, taking the respective values of $f$, this ratio becomes

$$\gamma\,(\text{monatomic}) = \tfrac{5}{3},$$

$$\gamma\,(\text{diatomic}) = \tfrac{7}{5},$$

and

$$\gamma\,(\text{triatomic}) = \tfrac{4}{3}$$

For more complex molecules with $f > 6$, $\gamma$ will be less than $\frac{4}{3}$ and may, in some cases, be nearer 1·1.

## 3.7. *The Einstein Diffusion Equation*

As a last application of the Maxwell–Boltzmann statistics to be considered in this chapter a relationship will be derived between the mobility $\mu$ and the diffusion coefficient $D$ of ions in a gas.

Consider a gas contained in a vessel with non-conducting walls. Let there be an electric field $E$ applied across the gas by means of charged plates outside the vessel as shown in Fig. 8 and let there be $n(x)$ ions per unit volume at a distance $x$ from the end of the vessel. If the charge on each ion is $q$ then the potential energy of an ion at $x$, compared with that of an ion at $x = 0$, will be

$$\epsilon(x) = -qEx$$

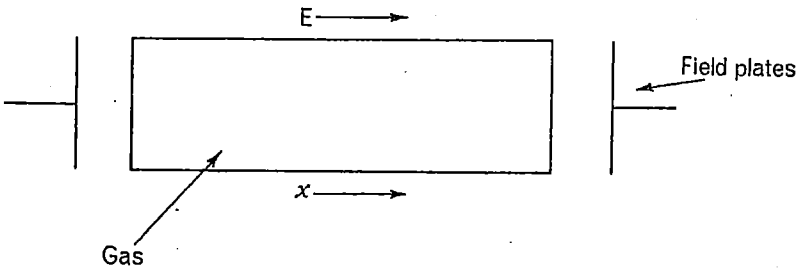


Fig. 8. Gas containing ions in electric field.

provided that the concentration of the ions is insufficient to affect the uniformity of the value of the electric field. Because of this energy gradient there will be a concentration gradient of ions in the gas. Using the Boltzmann factor for the relative probability that an ion will have a particular energy gives

$$\frac{n(x)}{n(0)} = e^{-\epsilon(x)/kT} = e^{qEx/kT} \qquad 3.42$$

where $n(0)$ is the concentration of ions at $x = 0$ and $T$ is the temperature of the gas.

Now, if the ions have a mobility $\mu$, there will be an ionic drift velocity $\mu E$ in the direction of the field $E$. There will thus be a drift current of ions across the plane at $x$ equal to

$$j\,(\text{drift}) = n(x)\,.\,\mu E \qquad 3.43$$

per unit area per unit time.

Also, if $D$ is the diffusion coefficient for the ions, there will be a diffusion current of ions across unit area at $x$ which, by definition, is

$$j\,(\text{diffusion}) = -D\frac{dn(x)}{dx} \qquad 3.44$$

per unit time in the direction of the concentration gradient. However, since in the case under discussion there can be no total current flow, there can be no total movement of ions. Thus

$$j\,(\text{drift}) + j\,(\text{diffusion}) = 0$$

or, from equations 3.43 and 3.44,

$$n(x)\,.\,\mu E = D\frac{dn(x)}{dx} \qquad 3.45$$

Substituting for $n(x)$ from equation 3.42 gives

$$\frac{dn(x)}{dx} = n(x) \cdot \frac{qE}{kT}$$

so that equation 3.45 becomes

$$\mu = \frac{Dq}{kT}$$

or

$$\boxed{\frac{\mu}{D} = \frac{q}{kT}} \qquad 3.46$$

which is the Einstein Diffusion Equation.

## PROBLEMS

1. Derive the variation of pressure with height in a column of gas at temperature $T$, (*a*) using the fact that the change in pressure over a height $dh$ is $-\rho g\, dh$ where $\rho$ is the density of the gas and (*b*) using the Boltzmann factor to give the concentration gradient of the molecules.

2. Calculate the mean values of $|v_x|$ and $v_x^2$ (see section 3.3).

3. Show that the integration of equation 3.10 over all polar angles leads to the distribution in equation 3.8.

Chapter 4

# Bose-Einstein Statistics

After the derivation of the statistical distributions appropriate to assemblies of non-interacting classical systems it is necessary to consider the properties of assemblies in which the systems, still considered to be non-interacting, obey the laws of quantum mechanics. In the present chapter consideration will be given to the statistics of *bosons* which are, as explained in section 1.4, quantum mechanical systems having integral angular momentum in units of $h/2\pi$ and which, therefore, do not obey the Pauli exclusion principle.

From the point of view of statistical mechanics the principal difference between bosons and classical systems lies in the fact that any two identical bosons will be completely indistinguishable. Thus, while the interchange of two 'identical' classical systems can lead to a new arrangement within an assembly, the interchange of two identical bosons cannot. This difference will lead to a different result for the most probable energy distribution of the systems in an assembly.

Another difference between quantum mechanical and classical systems is in the discrete nature of the available energy states. In the classical statistics the distribution, derived on the assumption that the energies could be divided into discrete levels, was shown to be unchanged when the separation of the levels was allowed to tend to zero. In the quantum mechanical case the discrete energy states must necessarily be considered as if each available state occupies a definite volume of phase space. In Appendix 5 this volume is shown to be equal to $h^3$ per state* so that, in a volume of phase space $d\Gamma$, there will be $d\Gamma/h^3$ states.

* This volume $h^3$ may be considered to be a result of Heisenberg's uncertainty principle. Thus the smallest value of the product $dxdp_x$ which can be obtained by measurement of the change of position and momentum of a system is approximately equal to $h$. The smallest meaningful value of an element of phase space $dxdydzdp_xdp_ydp_z$ is therefore approximately $h^3$. Exact calculation shows that this smallest element of phase space is, in fact, equal to $h^3$ for a single state.

## 4.1. *The Bose–Einstein Distribution*

The most probable energy distribution for an assembly of identical, non-interacting bosons may be obtained by a method strictly similar to that which was used in the case of a classical assembly. The configuration of the assembly is again specified such that the sheet $s$, consisting of all the $g_s$ states with energies in the range $\epsilon_s$ to $\epsilon_s + d\epsilon_s$, contains $n_s$ systems. The limitations which are imposed on the allowed values of the occupation numbers $n_s$ again arise from the fixed energy $E$ and fixed number of systems $N$ of the assembly so that

$$\sum_s n_s \epsilon_s = E \qquad \text{and} \qquad \sum_s n_s = N \tag{4.1}$$

It is now required to find the number of different arrangements of the systems which correspond to a given configuration or set of occupation numbers. Because the systems are indistinguishable the interchange of two systems, whether between two sheets or between two energy states in the same sheet, will not produce a new arrangement. The only different arrangements which can be formed arise from the arrangement of the systems in the sheets among the states available in the sheets.

Consider the $g_s$ states of sheet $s$ as represented by the compartments shown in Fig. 9 where the systems and the states are shown arranged in a row. The $n_s$ systems are to be arranged among the $g_s$ states. The arrangement must clearly begin with a state on the left as shown and this state may be chosen in $g_s$ ways. The first

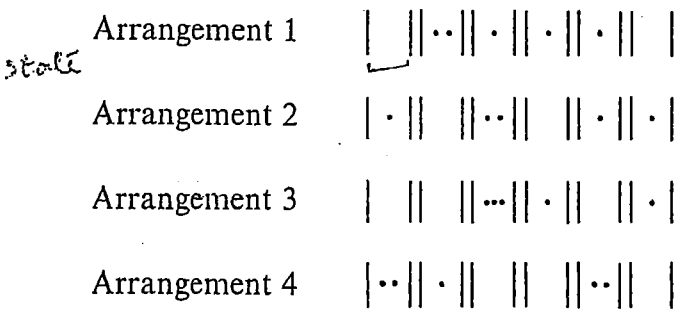


Fig. 9. Six states and five systems arranged in a row. The double lines represent the boundaries between the states and the dots represent the systems.

boundary of this first state may either have one of the $n_s$ systems or one of the remaining $(g_s - 1)$ states on its right and this system or state may be chosen in a total of $[(g_s - 1) + n_s]$ ways. The total

number of ways of positioning these $n_s$ systems and $(g_s-1)$ states after the first state has been chosen is thus $|(g_s-1)+n_s|!$ Together with the $g_s$ ways of selecting the first state, this gives

$$g_s|(g_s-1)+n_s|!$$

ways of arranging the $n_s$ systems among the $g_s$ states. However, this number includes the $g_s!$ arrangements of the states among themselves and the $n_s!$ arrangements of the indistinguishable systems. The number of distinguishable arrangements, $w_s$, of the systems within the sheet $s$ is therefore

$$w_s = \frac{g_s|(g_s-1)+n_s|!}{g_s!\,n_s!}$$

$$= \frac{|(g_s-1)+n_s|!}{(g_s-1)!\,n_s!} \qquad 4.2^*$$

Now the arrangements of the systems within a given sheet are necessarily independent of the arrangements within any other sheet. Therefore any arrangement of the systems in one sheet can be taken together with any of the arrangements of the systems in any other sheet. The total number of arrangements for a given configuration of the assembly, the weight of the configuration is thus

$$W = \prod_s w_s$$

$$= \prod_s \frac{|(g_s-1)+n_s|!}{(g_s-1)!\,n_s!} \qquad 4.3$$

As in the Maxwell–Boltzmann statistics the most probable configuration is determined by finding the values of $n_s$ which give a maximum value for the weight $W$. With the conditions from equation 4.1 introduced by means of Lagrange undetermined multipliers, this maximum is given, as in equation 2.15, by

$$\sum_s \left(\frac{\partial \log W}{\partial n_s}+\alpha+\beta\epsilon_s\right) dn_s = 0 \qquad 4.4$$

* Not surprisingly this result simply gives the number of ways of arranging the $n_s$ identical systems and $(g_s-1)$ identical bondaries between the states which are illustrated in Fig. 9 by the dots and the double lines respectively. Thus there are, in Fig. 9, ten objects to be arranged and these are made up of five identical dots and five identical double lines. The number of distinguishable arrangements is then 10!/5!5! which is equivalent to equation 4.2.

Since, at the maximum, this equation must be true for all small values of $dn_s$ then, as explained, the term in the brackets must be zero for all values of $s$. That is

$$\frac{\partial \log W}{\partial n_s} + \alpha + \beta\epsilon_s = 0 \qquad 4.5$$

If it is assumed that the number of states in each sheet is chosen to be sufficiently large to allow both $g_s!$ and $n_s!$ to be given by Stirling's approximation (see Appendix 2) then $\log W$ is obtained from equations 4.3 as

$$\begin{aligned} \log W &= \sum_s \log w_s \\ &= \sum_s [(g_s - 1 + n_s)\log(g_s - 1 + n_s) \\ &\quad -(g_s - 1)\log(g_s - 1) - n_s \log n_s] \end{aligned} \qquad 4.6$$

From this equation is obtained

$$\frac{\partial \log W}{\partial n_s} = \log(g_s - 1 + n_s) - \log n_s$$

and, since it has been assumed that both $g_s$ and $n_s$ are very much greater than unity,

$$\frac{\partial \log W}{\partial n_s} = \log\left(\frac{g_s + n_s}{n_s}\right) \qquad 4.7$$

Substituting from equation 4.7 into equation 4.5 gives

$$\log\left(\frac{g_s + n_s}{n_s}\right) + \alpha + \beta\epsilon_s = 0$$

and the most probable configuration is given when

$$\frac{g_s}{n_s} = e^{-(\alpha + \beta\epsilon_s)} - 1$$

Then

$$\boxed{n_s = \frac{g_s}{e^{-(\alpha + \beta\epsilon_s)} - 1}} \qquad 4.8$$

which is the general form of the Bose–Einstein distribution for an assembly of bosons.

If the general thermodynamic arguments of section 2.5 are applied in the determination of the multiplier $\beta$ it will be seen that, once again, it is possible to make the identification $\beta = -1/kT$. (The relation between the multiplier $\beta$ and the mean energy per system is not so easily determined in this case!) If the substitution $A = e^{\alpha}$ is also made, then equation 4.8 becomes

$$n_s = \frac{g_s}{\frac{1}{A}e^{\epsilon_s/kT} - 1} \qquad 4.9$$

and the average number of systems in the single state $i$ with energy $\epsilon_i$ is

$$\overline{n_i} = \frac{1}{\frac{1}{A}e^{\epsilon_i/kT} - 1} \qquad 4.10$$

The evaluation of the multiplier $\alpha$ by the application of the condition $\sum_s n_s = N$ from equation 4.1 is more complicated here than in the classical case and will be treated under the appropriate sections.

## 4.2. *The Bose–Einstein Gas*

If the molecules in an ordinary gas have integral angular momentum in units of $h/2\pi$ then they are, strictly speaking, bosons and they will obey the Bose–Einstein statistics. The distribution of the gas molecules over the various energy sheets will therefore be given by equation 4.9.

Since each allowed state requires a volume $h^3$ of phase space the weight of a sheet, the states of which may be considered to occupy a volume $d\Gamma$ of phase space, will be

$$g = \frac{d\Gamma}{h^3} \qquad 4.11$$

Appendix 4 (equation A4.7) gives the volume of phase space in the energy range $\epsilon$ to $\epsilon + d\epsilon$ as $2\pi(2m)^{\frac{3}{2}}\epsilon^{\frac{1}{2}}\,d\epsilon\,.\,V$ for a volume $V$. The number of available energy states in this energy range is therefore given by

$$g(\epsilon)\,d\epsilon = \frac{2\pi(2m)^{\frac{3}{2}}\epsilon^{\frac{1}{2}}\,d\epsilon\,.\,V}{h^3} \qquad 4.12$$

with $g(\epsilon)$ as the density of states. The number of molecules having energies in the range $\epsilon$ to $\epsilon+d\epsilon$ is then given by equations 4.9 and 4.12 as

$$n(\epsilon)\,d\epsilon = \frac{1}{h^3}\frac{2\pi(2m)^{\frac{3}{2}}\epsilon^{\frac{1}{2}}\,d\epsilon\,.\,V}{\frac{1}{A}e^{\epsilon/kT}-1} \qquad 4.13$$

The value of the parameter $A$ in this distribution may be determined from the condition that

$$\int_0^\infty n(\epsilon)\,d\epsilon = N \qquad 4.14$$

where $N$ is the total number of molecules in the volume $V$. In general this integral is difficult to evaluate exactly but it will be seen that, in most practical cases, the value of $A$ for the gas is sufficiently small to allow the term unity in the denominator of equation 4.13 to be ignored. When this condition is satisfied the distribution will approximate to the Maxwell–Boltzmann distribution and, because the molecules will be well spread out among the energy states, the gas is said to be non-degenerate. The integration of equation 4.14 then gives the same result as equation 2.55 except that the constant of proportionality $B$ is replaced by $h^{-3}$ so that

$$A = \frac{Nh^3}{V(2\pi mkT)^{\frac{3}{2}}} \qquad 4.15$$

and

$$\alpha = \log A = \log\left\{\frac{Nh^3}{V(2\pi mkT)^{\frac{3}{2}}}\right\} \qquad 4.16$$

Since the exponential $e^{\epsilon/kT}$ is greater than (or equal to) unity for all values of the energy the condition that equation 4.13 will approximate to the classical distribution is simply that equation 4.15 gives $A \ll 1$. If the values of $N$, $V$ and $m$ for helium* gas are substituted in equation 4.15 then, for standard atmospheric pressure;

$$\text{at } T = 300°\text{K}, \qquad A \simeq 3\times10^{-6}$$
$$\text{and at } T = 4°\text{K}, \qquad A \simeq 0{\cdot}15$$

Thus, even at 4°K, the condition $(1/A)\,e^{\epsilon/kT} \gg 1$ is fairly well satisfied and the helium gas will behave, to good approximation, as a classical gas.

* The common isotope of helium is composed of four nucleons and two electrons and therefore, having integral angular momentum, behaves as a boson.

THE EINSTEIN CONDENSATION

If the value of $A$ is increased towards unity it is no longer possible to treat the boson gas as if it behaved classically since the condition $(1/A)\,e^{\epsilon/kT} \gg 1$ will only hold for the high energy molecules. In this case account must be taken of the existence of an allowed state at the energy $\epsilon = 0$. Thus, while the distribution of the energy states given in equation 4.12 predicts that $g(0) = 0$, there will actually be one allowed state at the zero of energy. It is therefore possible to write the distribution of the molecule energies so that the total number $N$ is made up as

$$N = \frac{1}{\frac{1}{A}-1} + \int_0^\infty \frac{g(\epsilon)\,d\epsilon}{\frac{1}{A}\,e^{\epsilon/kT}-1} \qquad 4.17$$

$$= N_0 + N'$$

where $N_0 = 1/[(1/A)-1]$ is the number of molecules in the lowest energy state and $N'$ is the number of molecules with energies above this lowest state. As the value of $A$ increases towards unity the number $N_0$ will increase to include a large fraction of all the molecules.

This increase in the value of $N_0$ represents a reduction in the volume of momentum space occupied by the lower energy molecules and, by analogy with the normal condensation process in which there is a reduction of the volume of Euclidean space occupied by the molecules, this increase in $N_0$ is called an *Einstein condensation.* Such a condensation may occur either as the temperature $T$ is decreased or as the volume $V$ is reduced by the application of a high pressure. Thus the superfluid behaviour of the boson fluid liquid helium isotope $^4$He below 2·19°K and the behaviour of the material in highly condensed stars are both thought to be influenced by this form of condensation in energy or momentum space.

## 4.3. *Black-body radiation: the Photon Gas*

The electromagnetic radiation which is present inside any constant temperature enclosure may be considered as an assembly of photons of various energies. Because the photons have integral angular momentum in units of $h/2\pi$ they will naturally behave as bosons and it may be assumed that a photon gas will have an energy

distribution given by the Bose–Einstein statistics. However, two points must be noted.

Firstly, because photons may be absorbed and re-emitted by the walls of the enclosure, the number of photons inside the enclosure is not fixed. Thus the condition $\sum_s n_s = N$, or $\sum_s dn_s = 0$, given in equation 4.1 is not imposed on the distribution and the multiplier $\alpha$ is identically zero (i.e. $A = e^{\alpha} = 1$).

Secondly, the energy of a photon is $h\nu$, where $\nu$ is the frequency of the radiation, and it is therefore convenient to express the energy distribution of the photons in terms of either the frequency or the wave-length of the photons. It is shown in Appendix 5 (equation 5.10) that the number of independent wave modes in the wave-length range $\lambda$ to $\lambda + d\lambda$ is $(4\pi/\lambda^4)\, d\lambda$ per unit volume of the enclosure. However, in the photon gas, there are two independent directions of polarization of the electromagnetic wave, these directions being perpendicular to the direction of propagation of the wave. Each photon may have one of these directions of polarization and the number of allowed modes is therefore doubled. The number of allowed states, or modes, in the range $\lambda$ to $\lambda + d\lambda$ is thus

$$g(\lambda)\, d\lambda = \frac{8\pi}{\lambda^4}\, d\lambda \qquad 4.18$$

per unit volume where $g(\lambda)$ is the density of states in terms of the wave-length. Taking the Bose–Einstein distribution from equation 4.9 with $A$ equal to unity and the energy as $h\nu_s$ for the sheet $s$ gives the number of photons in this sheet at temperature $T$ as

$$n_s = \frac{g_s}{e^{h\nu_s/kT} - 1} \qquad 4.19$$

Then the number of photons, $n_\lambda(\lambda)d\lambda$, with wave-lengths in the range $\lambda$ to $\lambda + d\lambda$ is given, on substituting $g(\lambda)\, d\lambda$ from equation 4.18 for $g_s$ and writing $h\nu = hc/\lambda$, by

$$n_\lambda(\lambda)\, d\lambda = \frac{8\pi}{\lambda^4} d\lambda \cdot \frac{1}{e^{hc/k\lambda T} - 1} \qquad 4.20$$

where $c$ is the velocity of light.

The spectral distribution of the energy in the photon gas may be defined in terms of $E(\lambda)$, the energy of the radiation per unit volume per unit wave-length range at wave-length $\lambda$. Then, noting

that $E(\lambda) = n_\lambda(\lambda)h\nu = n_\lambda(\lambda)(hc/\lambda)$ because the energy per photon is $h\nu$, the energy of the radiation in the wave-length range $\lambda$ to $\lambda + d\lambda$ will be

$$E(\lambda)\,d\lambda = \frac{8\pi hc\,d\lambda}{\lambda^5(e^{hc/k\lambda T}-1)} \qquad 4.21$$

The expression in equation 4.21 is known as the *Planck Radiation Law* for the spectral distribution of the energy of radiation inside a constant temperature enclosure. The form of $E(\lambda)$ as a function of the wave-length $\lambda$ and also of the temperature is shown in Fig. 10.

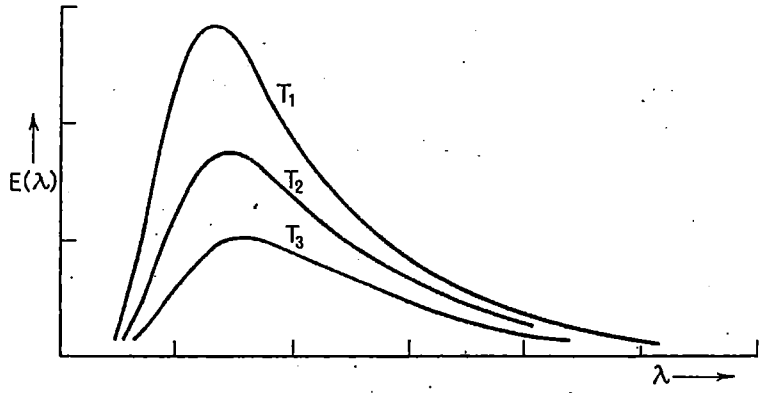


Fig. 10. The spectral distribution of radiant energy for temperatures $T_1 > T_2 > T_3$.

The following observations may be made concerning equation 4.21.

(*a*) The expression for $E(\lambda)$ is of the form $(1/\lambda^5)f(\lambda T)$ which is predicted by the Wien Radiation Law on purely thermodynamic arguments.

(*b*) At long wave-lengths, i.e. where $e^{hc/k\lambda T} \simeq 1 + hc/k\lambda T$, the equation 4.21 reduces to

$$E(\lambda)\,d\lambda \simeq \frac{8\pi kT\,d\lambda}{\lambda^4} \qquad 4.22$$

which is in agreement with the classical Rayleigh–Jeans formula* derived on the assumption that each of the $(8\pi/\lambda^4)\,d\lambda$ photons has the classical harmonic oscillator energy $kT$ (see equation 3.33).

* It should be noted that, contrary to experiment, this classical formula predicts an infinite value for the energy $E(\lambda)$ when $\lambda = 0$!

(*c*) At short wave-lengths, i.e. where $e^{hc/k\lambda T} \gg 1$, the equation 4.21 reduces to

$$E(\lambda)\,d\lambda \simeq \frac{8\pi hc}{\lambda^5} e^{-hc/k\lambda T}\,d\lambda \qquad 4.23$$

which is the Wien Distribution Formula that was originally proposed as an empirical fit for the experimental results at short wave-lengths.

(*d*) If a small hole is made in the side of the constant temperature enclosure some of the electromagnetic energy will be radiated out from the enclosure. Now it is known from kinetic theory that in a gas with $n$ molecules per unit volume the number of molecules impinging on a unit area in unit time is $\frac{1}{4}n\bar{v}$, where $\bar{v}$ is the mean velocity of the molecules. Then, if there is no particular wave-length selection in the absorption or emission of radiation by the hole (i.e. the hole acts as a black-body radiator) the number of photons emitted in the wave-length range $\lambda$ to $\lambda+d\lambda$ per unit area of the hole per unit time, $n_{\text{rad}}(\lambda)\,d\lambda$, can be taken as

$$n_{\text{rad}}(\lambda)\,d\lambda = n_\lambda(\lambda)\,d\lambda \cdot \frac{c}{4}$$

Using equation 4.20 for the value of $n_\lambda(\lambda)$ then gives

$$n_{\text{rad}}(\lambda)\,d\lambda = \frac{2\pi c\,d\lambda}{\lambda^4(e^{hc/k\lambda T}-1)} \qquad 4.24$$

The energy radiated per unit area per unit time in the given wave-length range is clearly $(hc/\lambda) \times n_{\text{rad}}(\lambda)\,d\lambda$ and may be written as

$$E_{\text{rad}}(\lambda)\,d\lambda = \frac{2\pi hc^2\,d\lambda}{\lambda^5(e^{hc/k\lambda T}-1)} \qquad 4.25$$

(*e*) The total energy $E$ per unit volume of the constant temperature enclosure is obtained by integrating equation 4.21 over the whole range of wave-lengths. That is

$$E = \int_0^\infty E(\lambda)\,d\lambda$$

$$= \int_0^\infty \frac{8\pi hc\,d\lambda}{\lambda^5(e^{hc/k\lambda T}-1)} \qquad 4.26$$

$$= \frac{8\pi h}{c^3}\left\{\frac{kT}{h}\right\}^4 \int_0^\infty \frac{t^3\,dt}{e^t-1} \qquad 4.27$$

where the substitution $t = hc/k\lambda T$ has been made. Expanding the integrand as a series in $e^{-t}$ and integrating by parts gives

$$\int_0^\infty \frac{t^3\,dt}{e^t-1} = 6\sum_{n=1}^{\infty}\frac{1}{n^4} = \frac{\pi^4}{15}$$

where the $n$'s are the positive integers. Equation 4.27 then becomes

$$E = \left\{\frac{8\pi^5k^4}{15h^3c^3}\right\}T^4 \qquad 4.28$$

which is equivalent to the energy density of radiation given by the Stefan–Boltzmann law.

Stefan's law of radiation in the form of the energy radiated per unit area per unit time from a body at temperature $T$ is

$$E_{\text{rad}} = \sigma T^4$$

where $\sigma$ is Stefan's constant. This expression may be obtained either by integrating equation 4.25 or, as explained above, by multiplying equation 4.28 by $\frac{1}{4}c$ to give

$$\sigma = \frac{2\pi^5k^4}{15h^3c^2} \qquad 4.29$$

## 4.4. *The specific heats of solids: the Phonon Gas*

In the same way that the energy of the electromagnetic radiation is quantized in the form of *photons* so the energy of the elastic waves, or sound waves, inside a solid medium can be considered to be quantized in the form of *phonons*. The energy of a phonon of frequency $\nu$ is again $h\nu$ and, because the phonons have integral angular momentum, the assembly of phonons in the solid may again be treated as a boson gas. It will be seen that, in the present case, it is convenient to express the phonon distributions in terms of their frequencies. The number of phonons, $n_\nu(\nu)\,d\nu$, with frequency $\nu$ to $\nu+d\nu$ may then be written from the Bose–Einstein distribution of equation 4.9, with $\alpha$ again equal to zero, as

$$n_\nu(\nu)\,d\nu = \frac{g(\nu)\,d\nu}{e^{h\nu/kT}-1} \qquad 4.30$$

where $g(\nu)\,d\nu$ is the number of allowed modes, or states, for the phonons in the range $\nu$ to $\nu+d\nu$.

The form of the distribution of allowed states, $g(\nu)$, in equation 4.30 will necessarily be different from the distribution for the perfect gas of photons. Firstly, there are three possible senses of polarization for a phonon: one polarization longitudinal and two transverse relative to the direction of propagation. The velocities of propagation corresponding to the two types of polarization will be different since the former represents a compressional wave while the latter represents a shear wave. Secondly, the solid medium is not a continuum but is made up of discrete lattice points.

In order to obtain a relatively simple form for $n_\nu(\nu)\,d\nu$ in equation 4.30 it is necessary to make a reasonable approximation to $g(\nu)\,d\nu$. Such an approximation was given by Debye in the form*

$$\begin{aligned} g(\nu)\,d\nu &= C\nu^2\,d\nu, \quad \nu \leqslant \nu_m \\ g(\nu)\,d\nu &= 0, \qquad\quad \nu > \nu_m \end{aligned} \tag{4.31}$$

where $C$ is a constant depending on the velocities of the transverse and longitudinal waves. The maximum frequency $\nu_m$ is determined by the fact that, for each atom in the solid, there are only three independent modes of vibration and hence, for the assembly of $N$ atoms which forms the solid, there can be only $3N$ independent modes of oscillation, i.e. $3N$ phonons. (This is equivalent to assuming, for simplicity, that the solid consists of monatomic molecules.) Then

$$\begin{aligned} 3N &= \int_0^\infty g(\nu)\,d\nu = \int_0^{\nu_m} C\nu^2\,d\nu \\ &= \tfrac{1}{3}C\nu_m^3 \end{aligned}$$

or

$$C = \frac{9N}{\nu_m^3} \tag{4.32}$$

The form assumed for $g(\nu)$ is shown in Fig. 11. It is expected that this approximate distribution will be satisfactory for low frequency phonons which will 'see' the solid as being almost continuous but that it will show deviations from the true distribution particularly at high frequencies where the wave-length approaches

* The distribution proportional to $\nu^2\,d\nu$ follows logically from the $d\lambda/\lambda^4$ form already given since on substituting $c/\nu$ for $\lambda$ this becomes

$$\frac{d(c/\nu)}{(c/\nu)^4} = -\frac{\nu^2\,d\nu}{c^3}$$

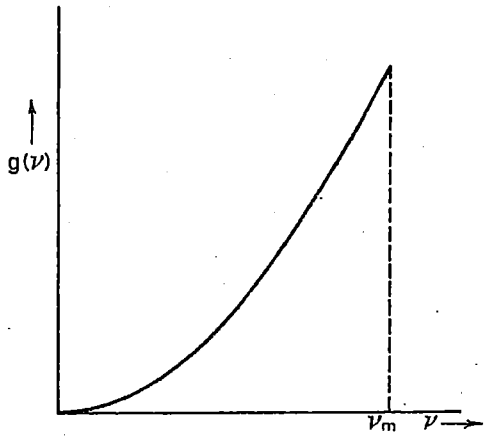


Fig. 11. The available states for phonons in a solid. The Debye approximation.

the atomic separation. On substitution from equations 4.31 and 4.32 in equation 4.30 the distribution of phonons becomes, on the Debye approximation,

$$\begin{aligned} n_\nu(\nu)\,d\nu &= \frac{9N}{\nu_m^3}\frac{\nu^2\,d\nu}{e^{h\nu/kT}-1}, \quad \nu \leqslant \nu_m \\ &= 0, \qquad\qquad \nu > \nu_m \end{aligned} \tag{4.33}$$

The energy $E$ of a gramme atom of a monatomic solid at temperature $T$ is obtained by setting the number of atoms $N$ equal to Avogadro's number $N_A$, putting the energy of the phonons in the frequency range $\nu$ to $\nu+d\nu$ as $n_\nu(\nu)h\nu\,d\nu$ and integrating over the frequency range 0 to $\nu_m$. Thus, using equation 4.33,

$$\begin{aligned} E &= \int_0^{\nu_m} h\nu n_\nu(\nu)\,d\nu \\ &= \frac{9N_A h}{\nu_m^3}\int_0^{\nu_m}\frac{\nu^3\,d\nu}{e^{h\nu/kT}-1} \end{aligned} \tag{4.34}$$

The specific heat of the solid is obtained by differentiating equation 4.34 with respect to the temperature $T$. If it is assumed that the limiting frequency $\nu_m$ remains constant as long as the volume of the solid is unchanged, then

$$C_v = \left\{\frac{\partial E}{\partial T}\right\}_v = \frac{9N_A h^2}{\nu_m^3}\frac{1}{kT^2}\int_0^{\nu_m}\frac{\nu^4 e^{h\nu/kT}\,d\nu}{(e^{h\nu/kT}-1)^2} \tag{4.35}$$

If the variable is changed to $x = h\nu/kT$ and $h\nu_m/k$ is replaced by $\theta_D$, the 'Debye characteristic temperature', equation 4.35 becomes

$$C_v = 9R\left\{\frac{T}{\theta_D}\right\}^3 \int_0^{\theta_D/T} \frac{x^4 e^x\, dx}{(e^x-1)^2} \qquad 4.36$$

where $R$, of course, replaces $N_A k$ and $x = \theta_D/T$ when $\nu = \nu_m$.

The specific heat given by equation 4.36 shows very good agreement with the form of the experimental curves even allowing for the simplification made in the initial assumptions. Also, as is found very nearly with the experimental curves, if the specific heat is plotted as a function of $(T/\theta_D)$ the curve will be the same for all monatomic solids, i.e. equation 4.36 represents a 'law of corresponding states'. The value of $\theta_D$ may, however, vary widely from solid to solid.

In the high temperature region where $\theta_D/T \ll 1$ it is possible to make the approximation $e^x \simeq 1+x \simeq 1$ in the integrand of equation 4.36. In this case the specific heat becomes

$$C_v \simeq 9R\left\{\frac{T}{\theta_D}\right\}^3 \int_0^{\theta_D/T} x^2\, dx.$$

$$= 3R$$

Thus, at these high temperatures, the Debye theory predicts that $C_v$ will be equal to the classical specific heat, in agreement with experiment.

In the low temperature region where $\theta_D/T$ is very large and $e^{-\theta_D/T} \ll 1$ equation 4.34 may be written with the upper limit of integration taken as $\theta_D/T \simeq \infty$ so that

$$C_v \simeq 9R\left\{\frac{T}{\theta_D}\right\}^3 \int_0^{\infty} \frac{x^4 e^x\, dx}{(e^x-1)^2}$$

Expanding the integrand in terms of $e^{-x}$ and successively integrating by parts gives

$$\int_0^{\infty} \frac{x^4 e^x\, dx}{(e^x-1)^2} = 24 \sum_{n=1}^{\infty} \frac{1}{n^4} = \frac{4\pi^4}{15}$$

where the $n$'s are the positive integers. Then

$$C_v \simeq \frac{12}{5}\pi^4 R\left\{\frac{T}{\theta_D}\right\}^3 \qquad 4.37$$

which is again in good agreement with experiment.

The variation of the Debye specific heat with temperature is shown in Fig. 12. To good approximation this form of the specific heat variation holds for a wide range of solids including most

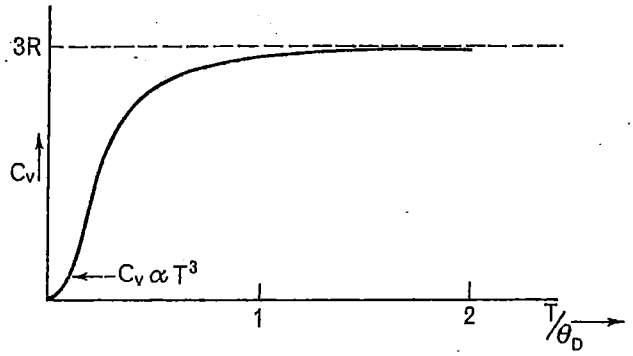


Fig. 12. Specific heat of a gramme atom of a solid—Debye theory.

metals and the alkali halides. Also the values of the Debye temperature $\theta_D$ calculated from the experimental curves are in good agreement with those calculated from the elastic constants of the solid through the constant $C$ in equation 4.31.

## PROBLEM

Using equation 4.20 show that the total number of photons per unit volume of an enclosure at temperature $T$ is

$$16\pi\left\{\frac{kT}{hc}\right\}^3 \sum_{n=1}^{\infty} \frac{1}{n^3}$$

where the $n$'s are positive integers.

Chapter 5

# Fermi-Dirac Statistics

While the Bose–Einstein statistics were developed to deal with those quantum mechanical assemblies consisting of bosons, the Fermi–Dirac statistics were developed for assemblies in which the systems have half-integral angular momentum and are therefore *fermions*. Because the fermions obey the Pauli exclusion principle then, as has been explained, the individual states which are available to the systems in a Fermi–Dirac assembly can be occupied by, at most, a single system. The form of the energy distribution for the assembly will be largely determined by this fact.

## 5.1. *The Fermi–Dirac Distribution*

Consider an isolated assembly consisting of $N$ non-interacting fermions and let the total energy of the assembly be $E$. As before, a particular configuration of the assembly may be expressed as a distribution of the systems over energy sheets. Thus the sheet $s$ is again considered to consist of all the $g_s$ states with energies in the range $\epsilon_s$ to $\epsilon_s + d\epsilon_s$. The given configuration is then specified by the values of $n_s$, the occupation numbers of the sheets for the various values of $s$. Because of the fixed number of systems and the fixed total energy the conditions

$$\sum_s n_s = N, \qquad \sum_s n_s \epsilon_s = E \tag{5.1}$$

are again imposed on the allowed values of the occupation numbers.

As in the case of bosons any rearrangement of the indistinguishable fermions among themselves will not produce a new, distinguishable arrangement. Therefore, if there are $w_s$ ways of arranging the $n_s$ systems in sheet $s$ among the $g_s$ states, the total number of arrangements corresponding to the given configuration will again be

$$W = \prod_s w_s \tag{5.2}$$

which is, of course, the weight of the configuration.

Because, by the exclusion principle, the occupation numbers of a single state can be only 0 or 1 then $n_s$ of the $g_s$ states in sheet $s$ will be occupied by a system and the other $(g_s - n_s)$ of the $g_s$ states will be empty. The number of arrangements of the systems in sheet $s$ can be taken either as the number of ways of arranging a sequence of $g_s$ states, of which $n_s$ are similar filled states and $(g_s - n_s)$ are similar empty states or, which is the same thing, as the number of ways of selecting the $n_s$ filled states from the $g_s$ states in the sheet. This gives, in both cases,

$$w_s = \frac{g_s!}{n_s!\,(g_s - n_s)!} \qquad 5.3$$

To illustrate this form of arrangement Fig. 13 shows diagrammatically the number of ways of arranging three filled states among a total of five states. It will be observed that the result is in agreement with equation 5.3.

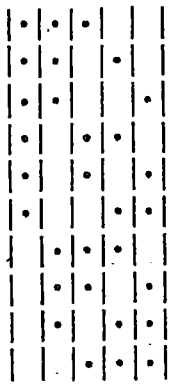

Fig. 13. The 5!/3!2! = ten ways of arranging five compartments (states) of which three are occupied by dots (systems) and two are empty.

The weight of the whole configuration is obtained by combining equations 5.2 and 5.3 to give

$$W = \prod_s \frac{g_s!}{n_s!\,(g_s - n_s)!} \qquad 5.4$$

Since the sheets are chosen to give values of $g_s$ and $n_s$ sufficiently large for the use of Stirling's approximation to be justified, equation 5.4 will give

$$\log W = \sum_s \log \frac{g_s!}{n_s!\,(g_s - n_s)!} \qquad 5.5$$

$$= \sum_s [g_s \log g_s - n_s \log n_s - (g_s - n_s)\log(g_s - n_s)]$$

Following equation 2.15, the condition for the most probable configuration is again given by

$$\sum_s \left\{ \frac{\partial \log W}{\partial n_s} + \alpha + \beta \epsilon_s \right\} dn_s = 0 \qquad 5.6$$

where the Lagrange undetermined multipliers, $\alpha$ and $\beta$, take account of the conditions imposed in equation 5.1. Since equation 5.6 must again be satisfied for all small values of $dn_s$ if $W$ is to be a maximum then, for all values of $s$,

$$\frac{\partial \log W}{\partial n_s} + \alpha + \beta \epsilon_s = 0 \qquad 5.7$$

If the thermodynamic arguments of section 2.5 are applied to equation 5.7 in order to determine the equilibrium state of two assemblies in thermal contact it will follow that the multiplier $\beta$ can be again identified as $-1/kT$.

Now, from equation 5.5,

$$\frac{\partial \log W}{\partial n_s} = \log \frac{g_s - n_s}{n_s} \qquad 5.8$$

so that equation 5.7 becomes

$$\log \frac{g_s - n_s}{n_s} + \alpha + \beta \epsilon_s = 0$$

that is,

$$\frac{g_s}{n_s} = e^{-(\alpha + \beta \epsilon_s)} + 1$$

The value of $n_s$ in the most probable configuration is then

$$\boxed{n_s = \frac{g_s}{e^{-(\alpha + \beta \epsilon_s)} + 1}} \qquad 5.9$$

which expression represents the Fermi–Dirac distribution for an assembly of fermions.

The term $1/(e^{-(\alpha + \beta \epsilon_s)} + 1)$ in equation 5.9 is generally known as the *Fermi function* and can be more conveniently written in the form

$$\boxed{f(\epsilon) = \frac{1}{e^{(\epsilon - \epsilon_F)/kT} + 1}} \qquad 5.10$$

where the substitutions $\beta = -1/kT$ and $\alpha = \epsilon_F/kT$ have been made and the suffix $s$ has been dropped. The energy $\epsilon_F$ occurring in this expression is known as the *Fermi energy*. On comparing equations 5.10 and 5.9 it is seen that this Fermi function gives the probability that a state with energy $\epsilon$ is occupied by a fermion and the energy $\epsilon_F$ is that energy for which this probability has the value one-half.

If, again, the number of states in the energy range $\epsilon$ to $\epsilon + d\epsilon$ is taken as $g(\epsilon)\,d\epsilon$, the distribution given in equation 5.9 may be written in terms of the number of systems in this energy range

$$n(\epsilon)\,d\epsilon = f(\epsilon)g(\epsilon)\,d\epsilon \qquad 5.11$$

## 5.2. *The Fermi–Dirac Gas*

Before a discussion can be given of the properties of a gas composed of fermions it is necessary to appreciate the significance of the Fermi energy $\epsilon_F$. Consider first the behaviour of the Fermi function given by equation 5.10 for the case when the assembly is at the absolute zero of temperature and the Fermi energy is $\epsilon_F(0)$.

When $T = 0$ the quantity $\{\epsilon - \epsilon_F(0)\}/kT$ has two possible values: for $\epsilon > \epsilon_F(0)$, $\{\epsilon - \epsilon_F(0)\}/kT = \infty$ while for $\epsilon < \epsilon_F(0)$, $\{\epsilon - \epsilon_F(0)\}/kT = -\infty$. There are therefore two possible values of the Fermi function:

$$\text{for } \epsilon < \epsilon_F(0), \quad f(\epsilon) = \frac{1}{e^{-\infty}+1} = 1$$
$$\text{for } \epsilon > \epsilon_F(0), \quad f(\epsilon) = \frac{1}{e^{\infty}+1} = 0 \qquad 5.12$$

Equation 5.12 implies that, at the absolute zero of temperature, the probability that a state with energy $\epsilon < \epsilon_F(0)$ is occupied is unity, i.e. such states are all occupied. Conversely, all states with energies $\epsilon > \epsilon_F(0)$ will be empty. The form of $f(\epsilon)$ at $T = 0$ is shown as a function of energy in Fig. 14.

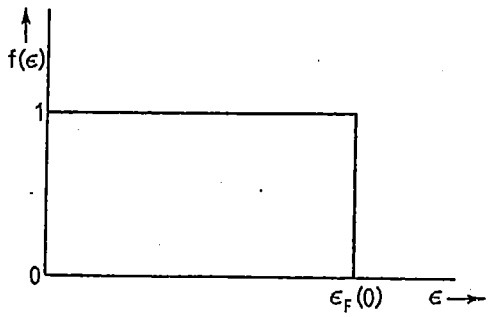


**Fig.** 14. The Fermi function at the absolute zero of temperature.

This behaviour of $f(\epsilon)$ may be explained very simply. At the absolute zero of temperature, the fermions will necessarily occupy the lowest available energy states. Thus, with only one fermion allowed per state, all the lowest states will be occupied until the fermions are all accommodated. The Fermi level, in this case, is simply the highest occupied state and above this energy level the states are unoccupied.

The value of $\epsilon_F(0)$ may be found from equation 5.11 by application of the condition that

$$\sum_s n_s = \int_0^\infty n(\epsilon)\, d\epsilon = N \qquad 5.13a$$

Because of the form of the Fermi function at $T = 0°K$, $n(\epsilon) = g(\epsilon)$ for $\epsilon \leqslant \epsilon_F(0)$ while $n(\epsilon) = 0$ for $\epsilon > \epsilon_F(0)$ so that this condition is equivalent to

$$\int_0^{\epsilon_F(0)} g(\epsilon)\, d\epsilon = N \qquad 5.13b$$

Since the fermions are quantum mechanical systems the form of the density of states $g(\epsilon)$ may be taken from equation 4.12 but with allowance made for the fact that the spin angular momentum of the fermions will result in more than one allowed state per energy level. Because of its wide application, e.g. in the case of electrons, it is usual to consider the case where the magnetic spin quantum number of the fermions has the two possible values $+\frac{1}{2}$ and $-\frac{1}{2}$. There will then be two states per energy level and

$$g(\epsilon) = V.4\pi\left\{\frac{2m}{h^2}\right\}^{\frac{3}{2}} \epsilon^{\frac{1}{2}} \qquad 5.14$$

for a volume $V$. Equation 5.13b then becomes

$$\int_0^{\epsilon_F(0)} V.4\pi\left\{\frac{2m}{h^2}\right\}^{\frac{3}{2}} \epsilon^{\frac{1}{2}}\, d\epsilon \equiv N$$

from which

$$\boxed{\epsilon_F(0) = \frac{h^2}{2m}\left\{\frac{3N}{8\pi V}\right\}^{\frac{2}{3}}} \qquad 5.15$$

In order that a convenient comparison may be made between the Fermi energy and the normal thermal energy $kT$, it is convenient

to define a Fermi temperature* $T_F$, such that

$$kT_F = \epsilon_F(0) \qquad 5.16$$

In Table I the values of $\epsilon_F(0)$ and $T_F$ are given for different Fermi–Dirac gases: the fermion gas formed by atoms of the helium isotope $^3_2$He at standard pressure and also the 'gas' of electrons in the alkali metals lithium and potassium. (For the purpose of the calculation of the Fermi energy it is assumed that the valence electrons of the alkali metals behave as a gas of free particles contained inside the potential well produced by the positive ions of the lattice.) The large difference between the Fermi energies for the $^3_2$He gas and the electron gases arises partly from the difference in the masses of the particles concerned and partly from the difference in the number of particles per unit volume in the two cases.

TABLE I: Fermi energies and temperatures

| Gas | $\epsilon_F(0)$ (eV) | $T_F$ (°K) |
|---|---|---|
| Helium ($^3_2$He atoms) | $0{\cdot}94 \times 10^{-3}$ | 10 |
| Electron gas in lithium | 4·7 | 54,000 |
| Electron gas in potassium | 2·1 | 24,000 |

For those molecular gases which consist of fermions the Fermi temperatures are low compared with normal room temperature. The effect of the Pauli exclusion principle on the energy distribution in these cases will therefore be small at ordinary temperatures. This follows because, except for the lowest energies, the average occupation of a state will be very much less than unity and, for those molecules having energies $(\epsilon - \epsilon_F) \gg kT$, the Fermi function will approximate very closely to the classical expression $\exp\{-(\epsilon - \epsilon_F)/kT\}$. The energy distribution of the gas molecules at room temperature will therefore approximate very closely to that for a classical Maxwell–Boltzmann gas.

In the case of an electron gas in a metal, the metal will have melted long before the energy $kT$ has approached the value of the Fermi energy. It is therefore necessary to treat the electron gas as a separate case.

## 5.3. *The Electron Gas*

Because of the high value of the Fermi temperature for the electron gas in a metal it is expected that an increase of the temperature

* Sometimes referred to as the Fermi degeneracy temperature.

$T$ from absolute zero to a value in the neighbourhood of room temperature will only affect those electrons with energies near the Fermi energy. This is demonstrated in Fig. 15 where it is assumed that $kT \ll \epsilon_F$ and the values of the Fermi function are included for the three particular cases:

$$\epsilon = (\epsilon_F - kT), \quad f(\epsilon) = \frac{1}{e^{-1}+1} \simeq 0{\cdot}73$$

$$\epsilon = \epsilon_F, \quad f(\epsilon) = \frac{1}{e^{0}+1} = 0{\cdot}5$$

$$\epsilon = \epsilon_F + kT, \quad f(\epsilon) = \frac{1}{e+1} \simeq 0{\cdot}27$$

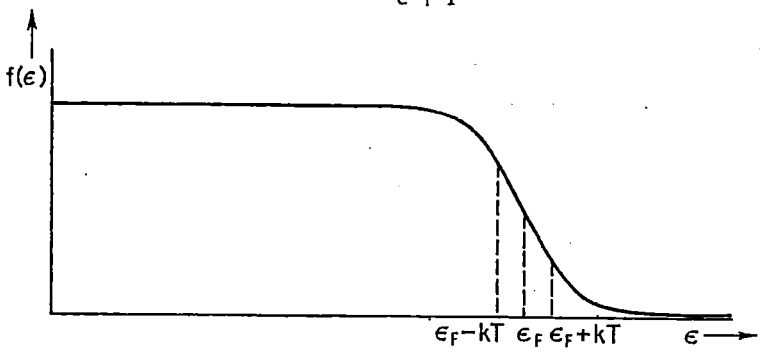


Fig. 15. Fermi function for $T_F \gg T > 0$.

Since the actual distribution of the electrons over the energies is that given by the product in equation 5.11, i.e.

$$n(\epsilon)\, d\epsilon = f(\epsilon) g(\epsilon)\, d\epsilon$$

with $g(\epsilon)$ as given in equation 5.14, the form of $n(\epsilon)$ will be that shown in Fig. 16 where the curve for $g(\epsilon)$ is also indicated.

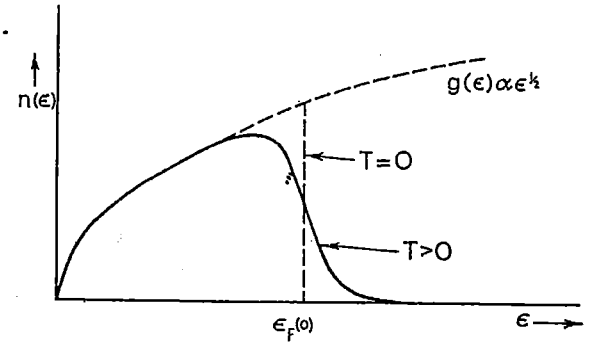


**Fig. 16. The distribution of electron energies for $T_F \gg T > 0$.**

At absolute zero the mean values of the various properties of the electrons may be calculated from the distribution integrals

with the limits taken as 0 and $\epsilon_F(0)$. For example, the mean energy of the electrons at $T = 0$ is given by

$$\bar{\epsilon}(0) = \frac{\int_0^\infty \epsilon n(\epsilon)\, d\epsilon}{\int_0^\infty n(\epsilon)\, d\epsilon}$$

so that, with $f(\epsilon) = 1$ for $\epsilon < \epsilon_F(0)$ and $f(\epsilon) = 0$ for $\epsilon > \epsilon_F(0)$,

$$\bar{\epsilon}(0) = \frac{\int_0^{\epsilon_F(0)} \epsilon g(\epsilon)\, d\epsilon}{\int_0^{\epsilon_F(0)} g(\epsilon)\, d\epsilon} = \tfrac{3}{5}\epsilon_F(0) \qquad 5.17$$

where use has been made of the value of $g(\epsilon)$ given in equation 5.14.

In order to find the effect on the distribution due to raising the temperature above the absolute zero it is necessary to obtain the value for the Fermi energy as a function of temperature. Using equation 5.11 the condition $\int_0^\infty n(\epsilon)\, d\epsilon = N$ becomes

$$\int_0^\infty f(\epsilon) g(\epsilon)\, d\epsilon = N \qquad 5.18$$

It is only necessary to evaluate this integral to determine the Fermi energy. Under the condition that $T \ll T_F$ a very good approximation may be obtained by using the fact that $df(\epsilon)/d\epsilon$ (or $f'(\epsilon)$) is only significantly different from zero in the neighbourhood of $\epsilon = \epsilon_F$. The details of the calculations are given in Appendix VII and only the main results will be presented here.

The Fermi level is given as a function of the temperature by the relation

$$\epsilon_F = \epsilon_F(0)\left[1 - \frac{\pi^2}{12}\left\{\frac{T}{T_F}\right\}^2\right] \qquad 5.19$$

where, for $T_F \sim 30{,}000°K$, the term $\frac{\pi^2}{12}\left\{\frac{T}{T_F}\right\}^2$ has a room temperature value of approximately $8 \times 10^{-5}$.

The mean energy of the electrons at temperature $T$ is obtained by evaluating the integral $\int_0^\infty \epsilon f(\epsilon) g(\epsilon)\, d\epsilon$ to give

$$\bar{\epsilon} = \epsilon_F(0)\left[\frac{3}{5} + \left\{\frac{T}{T_F}\right\}^2 \frac{\pi^2}{4}\right]$$

The constant volume specific heat of a 'mole' of the electron gas is given as $\partial(N_A\bar{\epsilon})/\partial T$, where $N_A$ is Avogadro's number, so that

$$C_v = \frac{\pi^2}{2}\frac{RT}{T_F} \qquad 5.20$$

With $T_F \sim 30{,}000°K$, the room temperature value of this specific heat will be approximately $0{\cdot}05R$. This must be compared with the value of $\frac{3}{2}R$ expected for the specific heat of a 'classical' electron gas, where each electron would have an energy $\frac{3}{2}kT$, and with the value of $3R$ for the lattice specific heat. (If it is required to determine the electronic specific heat experimentally the measurements must, in general, be made at low temperatures where the lattice specific heat falls off as $T^3$—see equation 4.37. At high temperatures the lattice specific heat will obscure that of the electron gas.)

## 5.4. *Pauli paramagnetism*

In the absence of any applied magnetic field there will be no net magnetic moment due to the spins of the electrons in a metal. However, when a magnetic field $H$ is applied to the metal, those electrons which have their spin magnetic moment parallel to the direction of the field will have a magnetic energy

$$\Delta\epsilon = 2\mu_B H \qquad 5.21$$

less than those which have their spin magnetic moments in the opposite direction, i.e. antiparallel to the field. (Here $\mu_B$, the Bohr magneton, is the magnetic moment due to the spin of the electron and in a magnetic field this moment may take up one of two positions, either parallel or antiparallel to the field.) Because of the difference in energy for the two spin states some of the electrons will reorientate themselves until more electrons have their magnetic moments parallel to the field than have them antiparallel.

The energy level diagrams for the two states of the electron spin at the absolute zero of temperature are shown in Fig. 17 where the density of states $g(\epsilon)$ is taken from equation 5.14 and the electrons with spin $+\frac{1}{2}$ are taken to have their moments antiparallel to the field $H$. The number of states is shown as $\frac{1}{2}g(\epsilon)$ since only half of the electrons will be in a given spin state. The electrons with spin $+\frac{1}{2}$ can be considered to have their energies increased by an amount $\mu_B H$ while those with spin $-\frac{1}{2}$ have their energies reduced by an equal amount.

It will be seen from Fig. 17(*b*) that, for equilibrium, those electrons with spin $+\frac{1}{2}$ and energy greater than $\epsilon_F(0)$ must reorientate themselves to give the configuration in Fig. 17(*c*). Because $\mu_B H \ll \epsilon_F(0)$ for all ordinary magnetic fields the number of electrons, $\Delta n$, involved in this reorientation may be approximated very closely

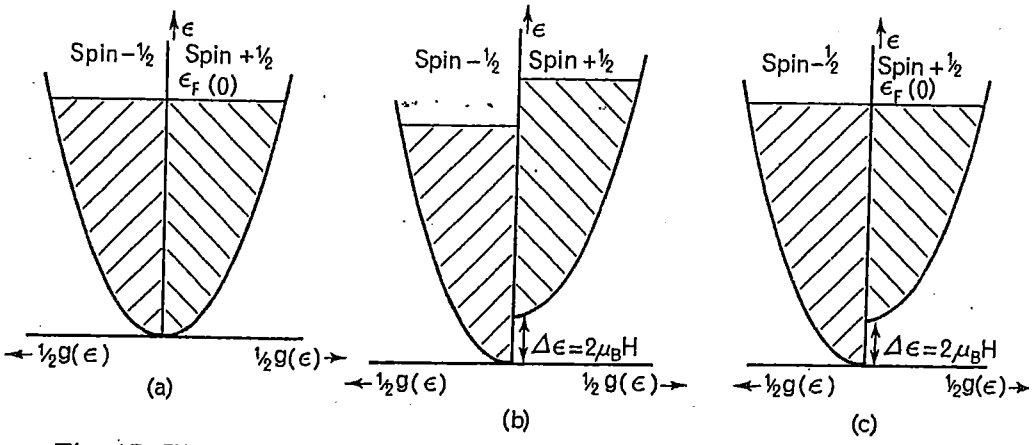


Fig. 17. The variation of the energy levels with applied magnetic field. (Occupied states are shown shaded.) (*a*) Distribution of electrons among the energy states at zero field. (*b*) Change in the energy states when a field $H$ is instantaneously applied. (*c*) Rearrangement of the electrons to the lowest energy states when the field is maintained at the value $H$.

by taking

$$\Delta n = \int_{\epsilon_F(0)}^{\epsilon_F(0)+\mu_B H} \tfrac{1}{2} g(\epsilon)\, d\epsilon \simeq \tfrac{1}{2} g(\epsilon_F(0))\mu_B H \qquad 5.22$$

Now each electron which is reorientated changes its moment from $-\mu_B$ to $+\mu_B$, i.e. a change of $2\mu_B$. The excess magnetic moment due to the rearrangement of the electrons is therefore simply

$$\begin{aligned} M &= \Delta n \,.\, 2\mu_B \\ &= \mu_B^2 H g(\epsilon_F(0)) \end{aligned} \qquad 5.23$$

The magnetic moment per unit volume of the electron gas is therefore

$$m = \frac{M}{V} = \mu_B^2 H \frac{g(\epsilon_F(0))}{V} \qquad 5.24$$

Because this moment is in the same direction as the applied magnetic field it will give a paramagnetic contribution to the total moment of the metal.

The paramagnetic susceptibility corresponding to equation 5.24 is

$$\chi_p = \frac{m}{H} = \mu_B^2 \frac{g(\epsilon_F(0))}{V} \qquad 5.25$$

Then substituting for $\epsilon = \epsilon_F(0)$ in equation 5.14 to obtain $g(\epsilon_F(0))$, this gives

$$\chi_p = \mu_B^2 4\pi \left\{\frac{2m}{h^2}\right\}^{\frac{3}{2}} \epsilon_F(0)^{\frac{1}{2}}$$

On using equation 5.15 to give the number of electrons per unit volume as

$$n = \frac{N}{V} = \frac{2}{3} \cdot 4\pi \left\{\frac{2m}{h^2}\right\}^{\frac{3}{2}} \epsilon_F(0)^{\frac{3}{2}}$$

this susceptibility becomes

$$\boxed{\chi_p = \frac{3}{2}\frac{n}{\epsilon_F(0)}\mu_B^2} \qquad 5.26$$

This form of paramagnetism is known either as *Pauli Paramagnetism* or, in order to distinguish it from the normal temperature dependent paramagnetism which is discussed in section 8.1, as *Temperature Independent Paramagnetism*. The only temperature dependence of $\chi_p$ is through the variation of the Fermi energy $\epsilon_F$, and this variation is negligible for ordinary temperature ranges.

(It should be noted that the susceptibility $\chi_p$ given by equation 5.24 is not the only contribution to the susceptibility of an electron gas. There is also a diamagnetic contribution of magnitude $-\frac{1}{3}\chi_p$, which arises from the translational motion of the electrons, besides the contributions from the cores of the positive ions.)

## 5.5. *Thermionic emission*

As already explained, the electron gas inside a metal may be considered to be contained inside a potential well. Figure 18(*a*) illustrates the form of such a potential well in one dimension, where the potential energy of an electron in the well is $-\epsilon_0$. If an electron is to escape from this metal, it must possess a kinetic energy $\epsilon_n$ greater than $\epsilon_0$ where $\epsilon_n$ is the component of the kinetic energy normal to a surface of the metal. The distribution, $n(\epsilon)$, of the electrons over the various energy states $\epsilon$ at an elevated temperature $T$ is shown in Fig. 18(*b*). The energy shown as $\phi$, the difference between $\epsilon_0$ and $\epsilon_F$, is known as the work function of the metal.

Consider the component velocities of the electrons in the neighbourhood of a metal surface which lies in the *yz*-plane as shown in

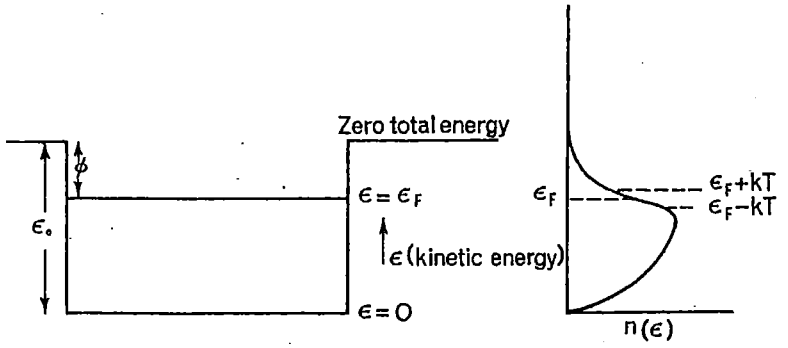


**Fig. 18(*a*). Electron energies in potential well of depth $\epsilon_0$.**

Fig. 18(*b*). Distribution $n(\epsilon)$.

Fig. 19. It is clear that only those electrons for which the velocity $v_x$ is towards the surface and for which

$$\epsilon_n = \tfrac{1}{2}mv_x^2 \geqslant \epsilon_0 \qquad 5.27$$

can escape from the metal and contribute to the thermionic emission of electrons.

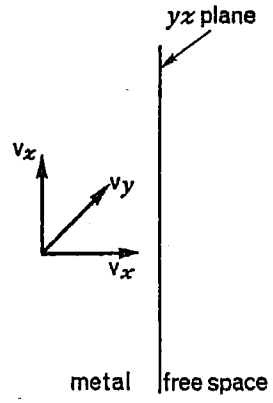


Fig. 19. Electron near the boundary of the metal.

The number of electrons per unit volume which have a component of velocity in the $x$-direction with a value between $v_x$ and $v_x + dv_x$, was shown in section 3.2 to be

$$n_x(v_x)\,dv_x = \left\{\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} n_3(v_x, v_y, v_z)\,dv_y dv_z\right\} dv_x \qquad 5.28$$

where $n_3(v_x, v_y, v_z)\,dv_x dv_y dv_z$ is the number of electrons per unit volume with velocity components in the range $v_x$ to $v_x + dv_x$, $v_y$ to $v_y + dv_y$, $v_z$ to $v_z + dv_z$. The Fermi–Dirac distribution function

in terms of the velocities may be written so that equation 5.9 gives

$$n_3(v_x, v_y, v_z)\, dv_x dv_y dv_z \equiv f(\epsilon)\frac{2d\Gamma}{h^3}$$

where the element of phase space $d\Gamma$ may be written in terms of the velocities as $m^3\, dv_x dv_y dv_z$ for unit volume, $f(\epsilon)$ is the Fermi function and the factor 2 arises from the two spin states of the electrons. Then, substituting from equation 5.10 for $f(\epsilon)$, this becomes

$$n_3(v_x, v_y, v_z)\, dv_x dv_y dv_z = \frac{2m^3}{h^3}\frac{dv_x dv_y dv_z}{e^{(\epsilon-\epsilon_F)/kT}+1} \qquad 5.29$$

Because only those electrons with energies in excess of the energy $\epsilon_0$ will contribute to the thermionic emission it is possible, to very good approximation for the present calculation, to ignore the term unity in the denominator of equation 5.29. Thus, with $\epsilon = \frac{1}{2}m(v_x^2+v_y^2+v_z^2)$, equation 5.29 becomes

$$\begin{aligned} n_3(v_x, v_y, v_z)\, dv_x dv_y dv_z \simeq{}& \frac{2m^3}{h^3}\exp(\epsilon_F/kT) \\ &\times \exp\{-\tfrac{1}{2}m(v_x^2+v_y^2+v_z^2)/kT\} \\ &\times dv_x dv_y dv_z \end{aligned} \qquad 5.30$$

Substituting in equation 5.28 gives

$$\begin{aligned} n_x(v_x)\, dv_x = {}& \frac{2m^3}{h^3}\exp(\epsilon_F/kT)\exp(-\tfrac{1}{2}mv_x^2/kT) \\ &\times\left\{\int_{-\infty}^{\infty}\exp(-\tfrac{1}{2}mv_y^2/kT)\, dv_y\right. \\ &\left.\times\int_{-\infty}^{\infty}\exp(-\tfrac{1}{2}mv_z^2/kT)\, dv_z\right\} dv_x \\ ={}& \frac{4\pi kTm^2}{h^3}\exp(\epsilon_F/kT)\exp(-\tfrac{1}{2}mv_x^2/kT)\, dv_x \end{aligned} \qquad 5.31$$

where use has been made of the integral $\int_{-\infty}^{\infty} e^{-\lambda x^2}\, dx = \sqrt{(\pi/\lambda)}$ as given in Appendix 6.

The number of electrons leaving the metal per unit area per unit time with the $x$-component of their velocity in the range $v_x$

to $v_x + dv_x$ will be

$$v_x n_x(v_x)\, dv_x$$

provided that, as given in equation 5.27, $\frac{1}{2}mv_x^2 \geqslant \epsilon_0$ and no reflection occurs at the metal boundary. The current per unit area, i.e. the current density carried by these electrons, will be

$$di = \varepsilon v_x n_x(v_x)\, dv_x \qquad 5.32$$

where $\varepsilon$ is the charge of the electron. The total current density is then

$$i = \int_{\frac{1}{2}mv_x^2 = \epsilon_0}^{\infty} \varepsilon v_x n_x(v_x)\, dv_x \qquad 5.33$$

which, on substituting from equation 5.31 for $n_x(v_x)\, dv_x$, becomes

$$i = \varepsilon \frac{4\pi kTm^2}{h^3} e^{\epsilon_F/kT} \int_{\frac{1}{2}mv_x^2 = \epsilon_0}^{\infty} e^{-\frac{1}{2}mv_x^2/kT} v_x\, dv_x$$

$$= \varepsilon \frac{4\pi k^2 T^2 m}{h^3} e^{\epsilon_F/kT} e^{-\epsilon_0/kT}$$

or

$$\boxed{i = A'T^2 e^{-\phi/kT}} \qquad 5.34$$

where $A' = 4\pi k^2 m\varepsilon/h^3$ and $\phi = (\epsilon_0 - \epsilon_F)$ is the work function of the metal. Equation 5.34 is known as the Richardson equation for the current density due to thermionic emission of electrons from a metal.

## PROBLEMS

1. Show that the mean velocity of an electron in an electron gas at the absolute zero of temperature is $\frac{3}{4}v_F$ where $v_F$ is the velocity of an electron at the Fermi energy.

2. Calculate the Fermi energy for the valence electrons in sodium metal given that the valency of sodium is one, the density of sodium is 0·97 g cm$^{-3}$, the mass of the electron is $9{\cdot}05 \times 10^{-28}$ g, Planck's constant is $6{\cdot}62 \times 10^{-27}$ erg sec, Avogadro's number is $6{\cdot}025 \times 10^{23}$ per gramme molecule and the atomic weight of sodium metal is 23. (Ans: $\epsilon_F(0) = 3{\cdot}12$ eV, $T_F \simeq 37{,}000$°K.)

3. Show that, for a gas in which the molecules behave as fermions, the value of the Fermi energy is approximately

$$\epsilon_F \simeq kT \log\left\{\frac{Nh^3}{V(2\pi mkT)^{\frac{3}{2}}}\right\}$$

for reasonably high temperatures. (See equation 2.56.)

Chapter 6

# Temperature and Entropy

In the previous chapters consideration has been given to the statistical nature of various thermodynamic assemblies and the discussion of the results arising from this statistical nature has been given without particular reference to the thermodynamic properties of the assemblies. However, two important thermodynamic functions have already entered into the statistical discussions: the total energy of the assembly and the temperature. Energy is, of course, a quantity common to both macroscopic assemblies and individual systems but the concept of temperature can only strictly have meaning when applied to the case of a macroscopic assembly. Because of this property of the temperature it will clearly be useful if, before progressing to a statistical treatment of the general thermodynamic functions, a discussion is given of the thermodynamic and statistical meaning of temperature. It will then be shown that the connection between the statistical and thermodynamic conceptions of a macroscopic assembly is established most easily through the consideration of the temperature and the entropy of the assembly.

Again the discussion will be restricted, in the main, to those assemblies in which the number of systems and the total energy are considered to be fixed. However, it will be seen that it is convenient to allow for fluctuations in the energy of the assemblies even though the main treatment of such fluctuations will not be given until the later chapters of the text.

## 6.1. *The statistical concept of temperature*

In section 2.5 it was shown how the Lagrange undetermined multiplier $\beta$, which occurs in equation 2.20, could be expressed as a function of the thermodynamic temperature with the aid of the 'zeroth' law of thermodynamics. Thus it was seen that any two assemblies, which were in thermodynamic equilibrium due to

their being in thermal contact, necessarily had the same value for $\beta$. Since the only criterion for thermodynamic equilibrium under this condition is that the temperatures of the two assemblies are equal it was clearly valid to express $\beta$ solely as a function of the thermodynamic temperature. It was also clear that the dependence of the multiplier $\beta$ on the temperature was the same whether the systems which composed the assembly obeyed Maxwell–Boltzmann, Bose–Einstein or Fermi–Dirac statistics. (It must be noted, however, that the dependence of the multiplier $\beta$ on the total energy of the assembly is not the same for the three types of systems.)

Once the temperature, and hence $\beta$, is fixed for a given assembly, so the form of the most probable distribution of the systems over the various energy sheets of the assembly will be determined. Conversely, once the form of this most probable distribution is determined so the multiplier $\beta$, and hence the temperature, will be a fixed quantity. The actual dependence of $\beta$ on the absolute temperature $T$, as defined on the perfect gas scale or Kelvin scale of temperature, was obtained in equation 2.41 by considering the properties of a Maxwell–Boltzmann gas. Thus it was shown that

$$\beta = -\frac{1}{kT} \tag{2.41}$$

where $k$ is Boltzmann's constant.

This relation may be taken as a definition of either $\beta$ or $T$ depending on which quantity is considered primarily to be fixed by the state of the assembly.

The statistical interpretation of the temperature of an assembly follows from the relationship which exists between the multiplier $\beta$ and the most probable configuration of the assembly. Two similar assemblies having the same total number of similar systems, the same total energy and the same volume will necessarily have the same thermodynamic temperature. The two assemblies will not, of course, necessarily have the same configuration at a given time but they will have the same *most probable* configuration. Also, if the two assemblies are placed in thermal contact so that energy may pass between them, there may be a finite transfer of energy from one assembly to the other at a given instant of time. There will, however, be no net transfer of energy when an average is taken over a sufficiently long period of time.

## 6.2. *Entropy*

In Chapter 2 the definition was given for the weight $W$ of a configuration of an assembly. It was shown in equation 2.13 that the condition that this weight shall have its maximum value can be written in the form

$$d \log W + \alpha\, dN + \beta\, dE = 0 \qquad (2.13)$$

where the terms $\alpha\, dN$ and $\beta\, dE$ take into account the restrictions on the total number of systems and on the total energy of the assembly. In the discussion of this equation it was noted that, in order for the quantity $d \log W$ to be a perfect differential, the multiplier $\beta$ should be proportional to the reciprocal of the absolute temperature $T$ and, as already mentioned, $\beta$ is actually taken as $-1/kT$. If an amount of heat $dQ$ is given to an assembly while both the volume of the assembly and the total number of systems are maintained constant then, since no work is done by the assembly, there will be an increase in the energy $dE$ equal to $dQ$. There will be a corresponding change in the weight $W$ of the most probable configuration, as given by equation 2.13 above, so that

$$d \log W + \beta\, dQ = 0 \qquad 6.1$$

On writing $\beta = -1/kT$ and remembering that the quantity $dQ/T$ is equal to $dS$, the gain in the entropy of the assembly, equation 6.1 gives

$$\boxed{dS = k\, d \log W} \qquad 6.2$$

This relation between the entropy and the weight of the configuration of an assembly may be considered as a differential form of the Boltzmann relation, $S = k \log W$, which is of great importance in the study of statistical thermodynamics. However, before this relationship is applied freely to problems in thermodynamics a somewhat fuller discussion is merited. For this purpose the following parallel properties of the entropy and the logarithm of the weight of the assembly configuration are noted.

(i) Consider two assemblies at the same temperature and pressure and consisting of identical non-interacting systems. Let the entropies of the two assemblies at a given instant of time be $S_1$ and $S_2$ and let the weights of the corresponding configurations

of the assemblies be $W_1$ and $W_2$. Now, if the two assemblies are considered as a combined assembly, the total entropy of the combination will be

$$S_T = S_1 + S_2 \qquad 6.3$$

At the same time the total weight of the configuration of the combined assembly will be

$$W_T = W_1 W_2 \qquad 6.4$$

since any of the $W_1$ arrangements of the first assembly can be taken together with any one of the $W_2$ arrangements of the second. If, therefore, it is assumed to be possible to write the entropy as some function of the weight of the assembly configuration, it is clear that the equations 6.3 and 6.4 will require that $S$ and $W$ satisfy a relationship of the form

$$S \propto \log W$$

The additive property of the entropy will then follow from equation 6.4 in the form

$$\log W_T = \log W_1 + \log W_2 \qquad 6.5$$

which will be equivalent to equation 6.3.

(ii) It is known from the Nernst heat theorem (the third law of thermodynamics) that as the temperature of a thermodynamic assembly tends to absolute zero so the entropy tends to zero also. Now, in the production of temperatures approaching the absolute zero, use is made of the process known as adiabatic demagnetization. In this process the electron spins of a paramagnetic salt are aligned by the application of a large magnetic field so that the ordering of the spins is increased. It is reasonable to assume that when the temperature of the spinning electrons reaches zero so the spins will be completely ordered, there being no thermal energy to displace them from their alignment along the magnetic field. The configuration of the spin assembly in this ordered state can only be formed in one way so that, with $W = 1$, the value of $\log W$ will be zero. The entropy of the spinning electrons, as given by the relation $S \propto \log W$, will also be zero for this case in agreement with the third law of thermodynamics.

(iii) From the second law of thermodynamics it is known that any spontaneous change which occurs in the state of an isolated

thermodynamic assembly will be accompanied by a change in entropy which will be positive or zero but never negative. Considered from the point of view of the weight of the assembly it is clear that a spontaneous change will only occur if the initial state of the assembly is less probable than, or has the same probability of occurrence as, the final state. Since the probability of a given configuration may be assumed proportional to its weight, the increase in entropy which occurs in the assembly will thus be accompanied by a change from a given configuration with a particular weight to one with a greater weight, as is expected from the proposed relation.

As an example of such a change consider a gas which is restricted by a partition to one half of a vessel, the other half of the vessel being evacuated. If the partition is removed it becomes possible for the molecules of the gas to occupy the whole of the vessel. Clearly the weight of a configuration in which the whole vessel is occupied will be much greater than a configuration in which the molecules remain in one half of the vessel. There will thus be a high probability, almost amounting to certainty, that the gas will undergo a spontaneous expansion to fill the whole vessel. This spontaneous expansion will be irreversible in the thermodynamic sense and the increase in the weight of the configuration will therefore be accompanied by an increase in entropy, as is expected.

(iv) Finally, consider the case of two dissimilar gaseous assemblies $A$ and $B$ which are separated by a partition as shown in Fig. 20($a$). Assume that assembly A is composed of the molecules $a$ and assembly B is composed of the molecules $b$. Let the entropy and configuration weight of assembly A be $S_A$ and $W_A$ respectively while the corresponding quantities for assembly B are $S_B$ and $W_B$. If the partition between the two assemblies is removed there will be no change in the energies of the assemblies as long as the

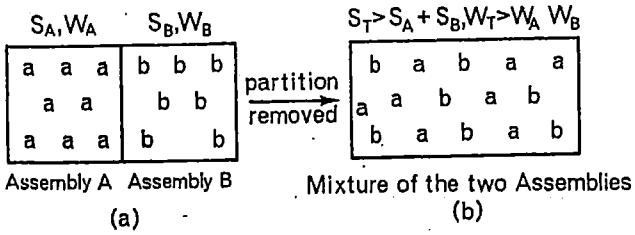


Fig. 20. The mixing together of two dissimilar gases.

temperatures and pressures of the two assemblies are equal and there is no interaction between the molecules. However, as the component molecules of one assembly diffuse into the region which was previously occupied by the other assembly alone, as shown in Fig. 20(*b*), there will be a change in the total entropy. Because the diffusion process is irreversible this entropy change will be positive and the final total entropy $S_T$ will show an increase over the combined entropies so that

$$S_T > S_A + S_B \qquad 6.6$$

Alternatively it may be considered that, since the removal of the partition allows both the molecules *a* and the molecules *b* to move over the whole of the volume, the total weight of the combined assemblies, $W_T$, will be greater than the simple product of the two weights $W_A$ and $W_B$. Thus, in agreement with equation 6.6, it is possible to write

$$W_T > W_A W_B$$

for the combined assemblies. The exact form of the 'mixing' term which leads to the increase in the entropy in this case will be discussed in greater detail in section 7.3.

Following the above discussion it is clear that equation 6.1 expresses a result which is in agreement with the laws of thermodynamics and also that it is possible to use the integral form of this equation as

$$S = k \log W \qquad 6.7$$

It follows from equation 6.7 that the entropy of an assembly in its equilibrium state will be given by the relation

$$\boxed{S = k \log W_{max}} \qquad 6.8$$

since the value $W_{max}$ corresponds to the most probable configuration of the assembly. The maximum of the weight $W$ was shown in section 2.4 to be sufficiently sharp to preclude, in general, any appreciable fluctuations from this equilibrium or most probable

state. Therefore, although the entropy of an assembly may exhibit small fluctuations from this most probable value, for most purposes the mean entropy may be considered to be given by the integral Boltzmann expression of equation 6.8.

While a justification of equations 6.7 and 6.8 has been attempted here, the student should realize that the principal justification for using these expressions is that, *a posteriori*, the results which are obtained by using these expressions are in good agreement with experiment.

(An alternative to the Boltzmann expression of equation 6.8 is the form given by Planck, namely,

$$S = k \log \Omega$$

where $\Omega$ is the total weight of the assembly being the sum of all the weights $W$ for all the possible configurations of the assembly for the given energy and number of systems. For the present purposes the difference between the quantities $\log W_{max}$ and $\log \Omega$ is negligible in view of the sharpness of the maximum of $W$ and hence equation 6.8 will be used almost exclusively, any distinction made between the two definitions being generally unprofitable. However, it should be noted that the arguments given above will apply equally to the Boltzmann and the Planck definitions and that, where it is necessary to make a distinction between the two definitions, the Planck form will normally be the most appropriate.)

So far the discussion given in this section has dealt with the association between the entropy of an assembly and the weight of the particular assembly configuration. It is sometimes useful, however, to consider the entropy as being determined by the state of disorder of the assembly or, which is equivalent, by our ignorance of the state of the assembly. For example, if the molecules of a gas are restricted by a partition so that they may occupy a small region of an otherwise evacuated vessel, then an observer will know that the positions of the molecules are within the limits set by the vessel and the partition. If the partition is removed, the gas can expand until the molecules are moving over the whole volume of the vessel and the knowledge of the positions of the molecules will be consequently reduced. The increase in the entropy associated with the movement of the molecules as they take up a more probable configuration will be accompanied by an increase in the

disorder of the gas and by an increase in the observer's ignorance of the positions of the gas molecules.*

A second example of the association between entropy and an observer's ignorance of the state of an assembly may be obtained by considering a narrow beam of molecules travelling with uniform velocity. Such a beam will be in a highly ordered state corresponding to a low degree of ignorance of the state of the molecules and, also, to a low value of entropy. If the molecules are allowed to enter through a small aperture into an enclosure in which they will be scattered to form a random gaseous assembly then the disorder, and consequently an observer's ignorance of the positions and momenta of the molecules, will be increased. Again the final disordered state will have a higher probability of occurrence, i.e. a greater weight, than the more ordered initial state and the ignorance of the state will accordingly correspond to a higher entropy as given by equation 6.7.

## 6.3. *The free energy*

With the temperature and entropy of an assembly known in terms of its statistical description it is also useful to relate certain other thermodynamic functions to the statistical properties. In particular it is of interest to consider the *Helmholtz free energy* of the assembly defined by the relation

$$F = E - TS \qquad 6.9$$

If an assembly undergoes a slight change of state *at constant temperature* so that the energy changes from $E$ to $E+dE$ while the

* This is not to say that the change from an ordered to a disordered state is completely irreversible. If the molecules are classical systems then there is no reason why their velocities may not be reversed at a given instant of time. If all the molecules did suffer such a reversal then the assembly would retrace its steps to the original and more ordered state which it had before the partition was removed. However, such a process has an extremely small probability of occurrence compared with the probability that the gas will remain in a disordered state. Moreover this more ordered state would last for such a short period that it would be almost impossible to detect its occurrence. In the case of a quantum mechanical assembly where the positions and momenta of the systems are necessarily uncertain such a reversal of the motions would be impossible to define. Thus, while the disordering is not 'statistically' irreversible, it may be considered to be thermodynamically irreversible.

entropy changes from $S$ to $S+dS$ then the change in this free energy will be

$$dF = dE - T\,dS \qquad 6.10$$

Now, from the first and second laws of thermodynamics, it is possible to obtain the inequality

$$T\,dS \geqslant dE + d\mathbf{W} \qquad 6.11$$

where $d\mathbf{W}$ is the work done by the assembly on its surroundings and the equality sign holds only for a thermodynamically reversible process. The corresponding change in the free energy may then be found by combining equations 6.11 and 6.10 to give

$$dF \leqslant -d\mathbf{W} \qquad 6.12$$

During the change the free energy $F$ will thus decrease by an amount equal to, or greater than, the work done by the assembly. In the absence of any such work being done by the assembly (i.e. $d\mathbf{W} = 0$) any *isothermal* change in the free energy will, therefore, be less than or equal to zero. The equilibrium state of the assembly, under these conditions, will thus be that in which the free energy has decreased to its minimum value since then any change in the parameters of the assembly will give the change in the free energy as

$$dF = 0 \qquad 6.13$$

and no work will be done by the assembly.

Once the temperature of an assembly is fixed the application of equation 6.13 will allow the equilibrium state of the assembly to be determined if the free energy is known in terms of the various thermodynamic parameters. An indication of such application is given in sections 8.4 and 8.5.

The usefulness of a knowledge of the free energy arises also from its relation to the other thermodynamic functions of the assembly. For example, consider a reversible change in an assembly such that the temperature changes by $dT$ and the only work done is that due to the expansion of the assembly as its volume increases by $dV$. The work done by the assembly in this case is $p\,dV$ where $p$ is the pressure exerted by the assembly and, with the equality sign used for the reversible process, equation 6.11 becomes

$$T\,dS = dE + p\,dV$$

With this value of $T\,dS$, and with the temperature allowed to vary, the change in the free energy is obtained from equation 6.9 as

$$dF = dE - T\,dS - S\,dT$$

$$= -p\,dV - S\,dT \qquad 6.14$$

From equation 6.14 it is then possible to express both the pressure and the entropy in terms of the free energy as

$$p = -\left\{\frac{\partial F}{\partial V}\right\}_T \qquad 6.15$$

and

$$S = -\left\{\frac{\partial F}{\partial T}\right\}_V \qquad 6.16$$

The equation 6.15 may be used to find the equation of state of the assembly which will give the pressure exerted by the assembly in terms of its volume and temperature.

The substitution of the entropy from equation 6.16 in equation 6.9 allows the free energy to be written as

$$F = E + T\left\{\frac{\partial F}{\partial T}\right\}_V$$

This expression may be rearranged to that the energy $E$ is expressed as a function of the free energy in the form

$$E = F - T\left\{\frac{\partial F}{\partial T}\right\}_V \qquad 6.17$$

$$= -T^2\left\{\frac{\partial (F/T)}{\partial T}\right\}_V \qquad 6.18$$

$$\equiv \left\{\frac{\partial (\beta F)}{\partial \beta}\right\}_V \qquad 6.19$$

where $\beta$ is, of course, $-1/kT$.

Finally, it is possible to express the specific heat of the assembly in terms of the free energy since, by definition,

$$C_v = \left\{\frac{\partial E}{\partial T}\right\}_V$$

and, substituting from equation 6.17,

$$C_v = -T\left\{\frac{\partial^2 F}{\partial T^2}\right\}_V \qquad 6.20$$

Alternatively

$$C_v = -k\beta^2\left\{\frac{\partial^2(\beta F)}{\partial\beta^2}\right\}_V \qquad 6.21$$

In the next chapter it will be seen how the free energy can be determined from a knowledge of the statistical distribution of the systems within the assembly. Also, because of the relationships given in the equations 6.15, 6.16, etc., it will be seen how the other properties of the assembly may be found once the free energy is known.

Chapter 7

# The Thermodynamics of Gases

In this chapter a discussion will be given of the thermodynamic functions of a perfect gas in which any interactions between the molecules, even those which occur during collisions between the molecules, are considered to have a negligible effect on the thermodynamic properties of the gas. It will be seen that anomalous results are obtained for the entropy and free energy of the gas if all the molecules are treated as being distinguishable, classical systems. In order to avoid these anomalies it is necessary to treat the gas in a 'semi-classical' manner in which it is assumed that all molecules of the same isotope are completely indistinguishable. It will also be seen to be convenient to introduce the quantity $1/h^3$ as the number of states per unit volume of phase space to replace the undefined constant of classical statistical mechanics.

Except for a brief digression in the final section the molecules will be considered, in this chapter, to be structureless particles.

## 7.1. *The weight $W_{\max}$ for a classical perfect gas*

As shown in equation 2.7 the weight of a given configuration of the molecules in a perfect gas which contains $N$ classical structureless molecules is

$$W = N! \prod_s \left\{ \frac{g_s^{n_s}}{n_s!} \right\} \tag{2.7}$$

where $n_s$ is the occupation number of the sheet $s$ and $g_s$ is the degeneracy of that sheet. Taking the energy of the sheet $s$ to be $\epsilon_s$ the occupation numbers for the most probable configuration are given by equation 2.20 as $n_s = g_s e^{\alpha + \beta \epsilon_s}$ where $\alpha$ and $\beta$ are already defined. The weight of this most probable configuration, $W_{\max}$, is

then obtained in logarithmic form by applying Stirling's approximation. Taking equation 2.7 to give

$$\log W = N \log N - N + \sum_s (n_s \log g_s - n_s \log n_s + n_s)$$

$$= N \log N + \left( \sum_s n_s \log \frac{g_s}{n_s} \right)$$

then the most probable configuration is obtained, on substituting from equation 2.20 for $g_s/n_s$, as

$$\log W_{\max} = N \log N + \sum_s n_s \log \{e^{-(\alpha + \beta \epsilon_s)}\}$$

$$= N \log N - \alpha \sum_s n_s - \beta \sum_s n_s \epsilon_s \qquad 7.1$$

Writing $N = \sum_s n_s$ and $E = \sum_s n_s \epsilon_s$ equation 7.1 becomes

$$\log W_{\max} = N \log N - \alpha N - \beta E \qquad 7.2$$

where $E$ is the total energy of the assembly. If the substitution is made for $e^{\alpha} = A$ so that $\alpha = \log A$ then, with $\beta = -1/kT$, equation 7.2 gives

$$\log W_{\max} = N \log N - N \log A + \frac{E}{kT}$$

$$= N \log \frac{N}{A} + \frac{E}{kT} \qquad 7.3$$

(Although in certain cases it is mathematically convenient to work with $\beta$ as the variable instead of $T$—see for example equations 6.19 and 6.21—it is not always convenient to use two alternative expressions for functions which depend on the thermodynamic temperature. The future results will therefore be presented, in general, in terms of the temperature $T$ while any simpler form involving $\beta$ may be given in parentheses.)

## 7.2. *The Boltzmann Partition Function*

In place of the ratio $N/A$ of equation 7.3 it will be found convenient to define a quantity $Z$ such that

$$Z = \frac{N}{A} \equiv \frac{\sum_s n_s}{e^{\alpha}}$$

Using the values of $n_s$ from equation 2.20 this becomes

$$Z = \frac{\sum_s g_s e^{\alpha - \epsilon_s/kT}}{e^{\alpha}}$$

or

$$\boxed{Z = \sum_s g_s e^{-\epsilon_s/kT}} \qquad 7.4$$

In this form $Z$ is known as the *Boltzmann partition function* (or simply as the *partition function*) of a system in the assembly. This terminology is used because, in this expression for $Z$, individual terms in the summation determine how the systems of the assembly are distributed, or partitioned, among the various energy sheets.

The form of equation 7.4 is perfectly general but it is sometimes useful to express the partition function in terms of the individual energy states which are available. If the energy of the $i$th state is taken to be $\epsilon_i$ then, since the weight of an individual state is unity,

$$\boxed{Z = \sum_i e^{-\epsilon_i/kT}} \qquad 7.5$$

(Because of the possibility of expressing the partition function in this form, $Z$ is sometimes referred to as the *sum over states* or the *state sum* for a system in the assembly. The symbol $Z$ is taken from the equivalent German expression *Zustandssumme*.)

The partition function which is defined by equations 7.4 and 7.5 is not one of the generally measurable or measured thermodynamic quantities nor does it appear in the normal thermodynamic equations. However, it does form an important bridge between the statistical expressions for the state of an assembly and the corresponding thermodynamic functions since these latter will be found to be given fairly simply in terms of the partition function.

Substituting for $Z = N/A$ in equation 7.3 gives the expression for the weight of the most probable configuration as

$$\log W_{\max} = N \log Z + \frac{E}{kT} \qquad 7.6$$

The entropy is then obtained with the aid of equation 6.8 as

$$S = k \log W_{max}$$

$$= Nk \log Z + \frac{E}{T} \qquad 7.7$$

(or, with $Nk$ replaced by the universal gas constant $R$ for a gramme molecule of the gas,

$$S = R \log Z + \frac{E}{T})$$

Substituting from equation 7.7 for the entropy in the expression $F = E - TS$ allows the Helmholtz free energy to be expressed in terms of the partition function as, simply,

$$\boxed{F = -NkT \log Z} \qquad 7.8$$

It is possible to obtain an expression for the total energy $E$ in terms of the partition function by direct substitution from equation 7.8 into the expression $E = -T^2\left\{\frac{\partial(F/T)}{\partial T}\right\}_V$ of equation 6.18. However, a more direct method is as follows:

The mean energy of a system in a classical assembly may be written as

$$\bar{\epsilon} = \frac{E}{N} = \frac{\sum_s n_s \epsilon_s}{\sum_s n_s} = \frac{\sum_s g_s e^{(\alpha - \epsilon_s/kT)} \epsilon_s}{\sum_s g_s e^{(\alpha - \epsilon_s/kT)}}$$

Then, cancelling the common term $e^{\alpha}$ and writing $\sum_s g_s e^{-\epsilon_s/kT} = Z$, this gives

$$\bar{\epsilon} = \frac{\sum_s g_s \epsilon_s e^{-\epsilon_s/kT}}{Z} \qquad 7.9$$

Now, by differentiation of equation 7.4,

$$\left\{\frac{\partial Z}{\partial T}\right\}_V = \frac{1}{kT^2} \sum_s g_s \epsilon_s e^{-\epsilon_s/kT}$$

so that equation 7.9 may be written

$$\bar{\epsilon} = \frac{kT^2\left\{\frac{\partial Z}{\partial T}\right\}_V}{Z}$$

$$= kT^2\left\{\frac{\partial \log Z}{\partial T}\right\}_V \qquad 7.10$$

The total energy of the assembly is then

$$E = N\bar{\epsilon}$$

or

$$\boxed{E = NkT^2\left\{\frac{\partial \log Z}{\partial T}\right\}_V} \qquad 7.11$$

(A simpler expression in terms of $\beta$ is obtained from equation 7.11 as

$$E = N\left\{\frac{\partial \log Z}{\partial \beta}\right\}_V$$

Substituting this value for $E$ in the equation 7.7 for the entropy gives

$$S = Nk\left[\log Z - \left\{\frac{\partial \log Z}{\partial \log \beta}\right\}_V\right]$$

while the free energy is simply

$$F = N\frac{\log Z}{\beta})$$

Referring again to the expression for the free energy in equation 7.8 it is seen that

$$\log Z = -\frac{F}{NkT}$$

or

$$Z = e^{-F/NkT} \qquad 7.12$$

Writing $F/N \equiv f$, the free energy per system, the partition function becomes

$$\boxed{Z = \sum_i e^{-\epsilon_i/kT} = e^{-f/kT}} \qquad 7.13$$

Finally it is noted that it is possible to obtain other thermodynamic functions in terms of the partition function by reference to the normal thermodynamic relationships. For example:

(i) the specific heat at constant volume is obtained with the aid of equation 7.11 as

$$C_v = \left\{\frac{\partial E}{\partial T}\right\} = Nk\left\{2T\frac{\partial \log Z}{\partial T} + T^2\frac{\partial^2 \log Z}{\partial T^2}\right\}_V$$

(ii) the pressure of the gas is obtained from equations 6.15 and 7.8 as

$$p = -\left\{\frac{\partial F}{\partial V}\right\}_T = NkT\left\{\frac{\partial \log Z}{\partial V}\right\}_T \qquad 7.14$$

## 7.3. *The Evaluation of the Classical Partition Function*

In the evaluation of the classical partition function it is possible to replace the summation over sheets in equation 7.4 by an integration over all possible energies. If the number of energy states in the energy range $\epsilon$ to $\epsilon + d\epsilon$ is written as in equation 2.47, i.e.

$$g(\epsilon)\, d\epsilon = BV\, 2\pi(2m)^{\frac{3}{2}}\epsilon^{\frac{1}{2}}\, d\epsilon$$

then the partition function becomes

$$\begin{aligned} Z &= \sum_s g_s\, e^{-\epsilon_s/kT} \\ &\equiv \int_0^\infty e^{-\epsilon/kT} g(\epsilon)\, d\epsilon \\ &= 2\pi\, BV(2m)^{\frac{3}{2}} \int_0^\infty \epsilon^{\frac{1}{2}}\, e^{-\epsilon/kT}\, d\epsilon \end{aligned}$$

From equations A5.9 and A5.10 of Appendix 5 the integral in this expression is

$$\int_0^\infty \epsilon^{\frac{1}{2}}\, e^{-\epsilon/kT}\, d\epsilon = (kT)^{\frac{3}{2}}\Gamma(\tfrac{3}{2}) = (kT)^{\frac{3}{2}}\frac{\sqrt{\pi}}{2}$$

so that

$$\boxed{Z = BV(2\pi mkT)^{\frac{3}{2}}} \qquad 7.15$$

as would be expected from the definition of $Z$ as $N/A$ (see

equation 2.55). Substituting for this value of $Z$ in equation 7.8 gives the free energy as

$$F = -NkT\log[BV(2\pi mkT)^{\frac{3}{2}}] \qquad 7.16$$

and the entropy of the gas is

$$S = -\left\{\frac{\partial F}{\partial T}\right\}_V$$

$$= Nk\log[BV(2\pi mkT)^{\frac{3}{2}}]+\tfrac{3}{2}Nk \qquad 7.17$$

Since equation 7.15 gives $\left\{\frac{\partial \log Z}{\partial T}\right\}_V = \frac{3}{2}\frac{1}{T}$, then the total energy of the gas of $N$ molecules is given by equation 7.11 as

$$E = \tfrac{3}{2}NkT \qquad 7.18$$

as is expected for a classical perfect gas.

In classical statistics the constant $B$ in the density of states is not determined and there is therefore an uncertainty in the classical partition function of an assembly. This uncertainty gives an indeterminate factor, which depends on the value of $\log B$, in both the free energy and the entropy of the assembly. However, there is no uncertainty in the energy or the specific heat of the assembly since these quantities depend only on the differential of $\log Z$ and any constant terms in $Z$ are therefore eliminated in these cases.

The equation of state of the classical perfect gas may be obtained from the partition function of equation 7.15 by the use of equation 7.14 so that, since $\{\partial \log Z/\partial V\}_T = 1/V$,

$$p = NkT\left\{\frac{\partial \log Z}{\partial V}\right\}_T$$

$$= \frac{NkT}{V} \qquad 7.19$$

Writing $Nk = R$ this gives the normal equation of state of a gramme molecule of a perfect gas, i.e.

$$pV = RT \qquad 7.20$$

with no indeterminate factors.

The thermodynamic quantities given so far have been derived on the assumption that the molecules of the gas are structureless and that they are all distinguishable. If the molecules are not

structureless the partition function will contain other energy terms than those due to purely translational motion and some aspects of these energy terms are discussed in section 7.6. (A more complete discussion of the case of the diatomic molecule is given in Chapter 8.) In particular the classical energy of the molecules will be increased above the value given in equation 7.18 depending on the increased number of degrees of freedom of the molecules when they are no longer structureless.

The effect of the assumed distinguishability of the molecules on the thermodynamic properties of the classical gas will now be considered.

## 7.4. *Gibbs' paradox*

If the entropy of a classical perfect gas is computed from equation 7.17 there is found to be a paradoxical result for the case when two equal volumes of the same gas are mixed together. Consider the two equal volumes of the same gas, being at the same temperature and pressure and containing the same number of molecules, which are shown as volume 1 and volume 2 in Fig. 21. If these two volumes separately each have an entropy $S$, the value of this entropy will be given by equation 7.17 as

$$S = Nk \log[BV(2\pi mkT)^{\frac{3}{2}}] + \tfrac{3}{2}Nk$$

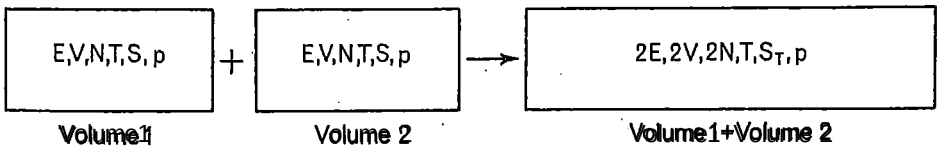


**Fig. 21. The mixing of two equal volumes of the same gas.**

**The total entropy** $S_T$, obtained by mixing together the two volumes, is given by replacing $N$ by $2N$ and $V$ by $2V$ while the temperature, being an intensive quantity (i.e. independent of the extension of the assembly) remains unchanged. Then

$$\begin{aligned} S_T &= 2Nk \log[B2V(2\pi mkT)^{\frac{3}{2}}] + \tfrac{3}{2} \cdot 2Nk \\ &= 2\{Nk[\log BV(2\pi mkT)^{\frac{3}{2}}] + \tfrac{3}{2}Nk\} + 2Nk \log 2 \\ &= 2S + 2Nk \log 2 \end{aligned} \qquad 7.21$$

From this equation it would appear that the removal of a partition from between two equal volumes of the same gas causes an increase in the total entropy and that this increase is given by the 'mixing term' $2Nk \log 2$ (or $2R \log 2$ for two gramme molecules).

Conversely, the replacing of the partition to recreate two separate, equal volumes of the same gas would presumably return the total entropy to its original value of $2S$. It would be expected, however, that the presence, or otherwise, of a partition between the two volumes would have no effect whatever on the entropy if the gas in each volume is the same. This apparently contradictory behaviour of the entropy is known as *Gibbs' paradox.*

It may be seen from closer study that there is, in fact, no real paradox in this phenomenon. Since the systems in a classical assembly, and hence the molecules in a classical perfect gas, are defined as being completely distinguishable from each other, then any two volumes of a classical gas must be taken to be completely dissimilar even if they are considered to be composed of molecules of the same isotope of the same element. In this case of complete distinguishability there is no difference in the entropy of mixing of the combined volumes whether they are considered to be, say, two equal volumes of oxygen or one volume of oxygen and one volume of nitrogen. (There will, however, be a difference in the individual entropies due to the dependence of the term $(2\pi mkT)^{\frac{3}{2}}$ in equation 7.17 on the mass of the molecules.) Thus, under this assumption, once the partition has been removed the original state cannot be restored by its being replaced.

The mixing term which occurs in equation 7.21 may be seen to arise from the increase in volume which is available to the molecules when the partition is removed. If the molecules were actually identical, so that the interchange of two molecules could not be detected, there would be no new configurations of the assemblies created by the removal of the partition. However, since the molecules have been considered to be classical, the removal of the partition will create, for each molecule, two possible positions in space for every single position which was available before. There are $N$ molecules in each volume and it follows that there will be $2^N$ times as many arrangements for the molecules of each volume as there were before the partition was removed. Thus, if the equilibrium weight of one of the assemblies when it occupies a volume $V$ is $W$, then the equilibrium weight of the assembly when it is allowed to expand into the volume $2V$ will be $W.2^N$.

If the total weight $W_T$ of the combined volume of gas is taken as the product of the individual weights then, on mixing,

$$W_T = (W.2^N)^2$$

Thus, with the entropy taken as $S = k \log W$ for each of the volumes independently, the total entropy becomes

$$S_T = k \log W_T$$
$$= 2k \log W + 2Nk \log 2$$
$$= 2S + 2Nk \log 2$$

in agreement with equation 7.21.

As has been pointed out, if the molecules in the two volumes were indeed identical the entropy of the combination would be simply $S_T = 2S$ and the removal or otherwise of the partition between the two volumes of the gas would have no effect on the total entropy. From this it is seen that there is necessarily an error in the expressions derived classically for the entropy, and also the free energy, of a perfect homogeneous gas composed of identical molecules. In the following section it is shown how this error can be eliminated if the gas molecules are treated in a 'semi-classical' manner.

(It is interesting to note that the same mixing term arises from the thermodynamic expressions for the entropy of a gramme molecule of a perfect gas, namely

$$S = C_v \log T + R \log V + \text{constant} \qquad 7.22$$

and

$$S = C_p \log T - R \log p + \text{constant} \qquad 7.23$$

where $C_p$ is the specific heat at constant pressure. If two equal volumes of gas at the same temperature and pressure are added together so that $C_p$, $C_v$, $R$ and $V$ must be replaced by $2C_p$, $2C_v$, $2R$ and $2V$ respectively then it is apparent that equation 7.22 will introduce a mixing term of $2R \log 2$ while equation 7.23 will not. The difference clearly arises from the fact that $V$ is an extensive quantity which depends on the amount of gas considered while $T$ and $p$ are intensive quantities which do not. While it is a useful rule in thermodynamics that equation 7.22 is used in computing the entropy of a mixture of two different gases and equation 7.23 is used for the entropy of two volumes of the same gas, it is only by the application of the statistical analysis that the problem can be properly resolved.)

## 7.5. *The semi-classical perfect gas*

It is possible to obtain a correct, consistent expression for the entropy of a real perfect gas by using the appropriate quantum

statistics. The actual statistics chosen will depend, strictly speaking, on whether the gas molecules are in fact bosons or fermions. However, in dealing with a gas at ordinary temperatures and pressures, it is mathematically convenient to go to the classical limit of these quantum statistics where the occupation number of each sheet, $n_s$, is small compared with the number of available levels, $g_s$. In this limiting case it will be seen that the three types of statistics give rise to the same result for the entropy and for the distribution of energies provided that the term $N!$ is removed from the weight of the classical assembly. It is necessary to remove this term $N!$ from the classical weight since this is the factor which gives the number of arrangements of the molecules among themselves and which, therefore, arises explicitly from the assumed distinguishability of the molecules.

The weight of the configuration of an assembly of 'semi-classical' systems is obtained by modifying equation 2.7 of the Maxwell–Boltzmann statistics to give

$$W_{\mathrm{MB}} = \prod_s \frac{g_s^{n_s}}{n_s!} \qquad 7.24$$

The corresponding weights for the Bose–Einstein and Fermi–Dirac distributions are

$$W_{\mathrm{BE}} = \prod_s \frac{(n_s+g_s-1)!}{n_s!\,(g_s-1)!} \qquad \text{(cf. 4.3)} \qquad 7.24'$$

and

$$W_{\mathrm{FD}} = \prod_s \frac{g_s!}{n_s!\,(g_s-n_s)!} \qquad \text{(cf. 5.4)} \qquad 7.24''$$

respectively. In the classical limit when $g_s \gg n_s \gg 1$ Stirling's approximation gives:

(i) $$\log W_{\mathrm{MB}} = \sum_s (n_s \log g_s - n_s \log n_s + n_s)$$

$$= \sum_s \left( n_s \log \frac{g_s}{n_s} + n_s \right) \qquad 7.25a$$

(ii) $$\log W_{\mathrm{BE}} \simeq \sum_s [(n_s+g_s)\log(n_s+g_s) - n_s \log n_s - g_s \log g_s]$$

$$= \sum_s \left[ n_s \log\left\{\frac{n_s+g_s}{n_s}\right\} + g_s \log\left\{\frac{n_s+g_s}{g_s}\right\}\right]$$

$$\simeq \sum_s \left( n_s \log \frac{g_s}{n_s} + n_s \right) \qquad 7.25b$$

where the approximations $(n_s+g_s-1) \simeq (n_s+g_s)$, $\frac{g_s+n_s}{n_s} \simeq \frac{g_s}{n_s}$ and $\log\left\{\frac{n_s+g_s}{g_s}\right\} = \log\left\{1+\frac{n_s}{g_s}\right\} \simeq \frac{n_s}{g_s}$ have been used.

(iii) $$\log W_{FD} = \sum_s [g_s \log g_s - n_s \log n_s - (g_s-n_s)\log(g_s-n_s)]$$

$$= \sum_s \left[ n_s \log\left\{\frac{g_s-n_s}{n_s}\right\} - g_s \log\left\{\frac{g_s-n_s}{g_s}\right\}\right]$$

$$\simeq \sum_s \left( n_s \log\frac{g_s}{n_s} + n_s \right) \qquad 7.25c$$

where approximations similar to those in (ii) have been introduced.

It is clear that under the conditions postulated here the weight of a given assembly is very nearly independent of the type of system of which the assembly is composed. The equilibrium energy distribution of the systems will therefore be very close to the Maxwell–Boltzmann form $n_s = g_s e^{\alpha - \epsilon_s/kT}$ for each case and the equilibrium entropy will be given by these values of $n_s$.

Taking $\log\frac{g_s}{n_s} = \left\{\frac{\epsilon_s}{kT} - \alpha\right\}$ the equations 7.25 give

$$\log W_{max} = \sum_s \left[ n_s \left\{\frac{\epsilon_s}{kT} - \alpha\right\} + n_s \right]$$

$$= \frac{E}{kT} - N\alpha + N$$

since $\sum_s n_s = N$ and $\sum_s n_s \epsilon_s = E$. The entropy of the assembly, $S = k \log W_{max}$, is thus

$$S = \frac{E}{T} - kN\alpha + kN \qquad 7.26$$

The constant $e^{\alpha} = A$ may be taken from equation 7.4 to be given by $N/Z$ so that $\alpha = \log(N/Z)$. The equation 7.26 can thus be written in terms of the partition function as

$$\boxed{S = Nk \log\frac{Z}{N} + \frac{E}{T} + Nk} \qquad 7.27$$

For a gas composed of structureless, semi-classical molecules the energy $E$ is simply the energy of translation $\frac{3}{2}NkT$. The partition function for the quantum assembly is given by equation 7.15 with the indeterminate factor $B$ replaced by $h^{-3}$, the quantum mechanical expression for the number of allowed states per unit volume of phase space.* That is

$$Z = \frac{V}{h^3}(2\pi mkT)^{\frac{3}{2}} \qquad 7.28$$

On substituting for the values of $E$ and $Z$ in equation 7.27, the entropy is obtained as

$$\boxed{S = Nk\left\{\log\left[\frac{V(2\pi mkT)^{\frac{3}{2}}}{Nh^3}\right] + \frac{5}{2}\right\}} \qquad 7.29$$

This expression is the *Sackur–Tetrode equation* for the entropy of a gas which has a volume $V$ and is composed of $N$ indistinguishable, structureless molecules at temperature $T$. In this expression the classical dependence of the entropy on the extensive variable $V$ is replaced by a dependence on the intensive variable $V/N$, which may be considered as the volume per molecule. Therefore, if two equal volumes $V$ of the same gas under the same conditions are added together to form a volume $2V$ then, since the volume per molecule remains unaltered, the mixing of the two volumes will produce no change in the total entropy as given by equation 7.29. If, however, the two volumes of gas consist of two different types of molecules then the mixing of the two volumes will increase the volume available to the two types of molecule from $V$ to $2V$. The volume per molecule will thus be doubled and there will be a corresponding increase in the total entropy due to the 'mixing' term, $2Nk \log 2$.

It is now possible to obtain an expression for the free energy $F$ for a perfect semi-classical gas. Using the form of the entropy

* In some texts the number of states per unit volume of phase space is assumed to be given by $h^{-3}$ for both quantum mechanical and classical systems. While this may be convenient, and it is certainly valid in the semi-classical case given here, in the strict classical limit this density of states, here given the symbol $B$, will tend to infinity.

from equation 7.27 in the expression $F = E - TS$ gives

$$F = -NkT \log \frac{Z}{N} - NkT$$

$$= -kT\{N \log Z - (N \log N - N)\}$$

Using Stirling's approximation this gives

$$F = -kT(\log Z^N - \log N!)$$

or

$$\boxed{F = -kT \log \frac{Z^N}{N!}} \qquad 7.30$$

The quantity $Z^N/N!$ is sometimes referred to as the *total partition function* of the assembly while the partition function $Z$ is taken as referring to an individual system. Giving the total partition function the symbol $\mathbf{Z}$ so that

$$\mathbf{Z} = \frac{Z^N}{N!} \qquad 7.31$$

then equation 7.30 for the free energy becomes

$$F = -kT \log \mathbf{Z} \qquad 7.32$$

The total partition function can thus be written as

$$\boxed{\mathbf{Z} = e^{-F/kT}} \qquad 7.33$$

(A further discussion of the properties of the total partition function will be given in Chapter 9 when the canonical ensemble is considered.)

It is left as an exercise for the student to show that the equation of state and the total energy of the gas, as derived from the free energy given in equation 7.30, are the same as those derived for the completely classical gas.

## 7.6. *Components of the Partition Function*

If the systems which make up an assembly are not structureless, the energies of the systems will not be due to their translational motion alone. Thus, in a gas consisting of polyatomic molecules, it is possible for the gas molecules to take energy in a number of

independent modes (e.g. vibrational, rotational and electronic energy modes) besides the normal translational mode.

Consider a system which has its energy state defined by three independent energies $\epsilon_1$, $\epsilon_2$ and $\epsilon_3$ which are, for example, the energies of translation, vibration and rotation. If the first form of motion is in its $i$th state with energy $\epsilon_{1i}$ and the second and third in the $j$th and $l$th states with energies $\epsilon_{2j}$ and $\epsilon_{3l}$ respectively, then the total energy $\epsilon_t$ will be

$$\epsilon_t(i,j,l) = \epsilon_{1i} + \epsilon_{2j} + \epsilon_{3l} \qquad 7.34$$

The partition function of the system in the assembly will then be

$$Z = \sum_{i,j,l} e^{-\epsilon_t(i,j,l)/kT} \qquad 7.35$$

where the sum must be taken over all possible values of $i$, $j$ and $l$ and all degenerate states are counted individually.* Substituting from equation 7.34 into equation 7.35 gives

$$\begin{aligned} Z &= \sum_{i,j,l} e^{-(\epsilon_{1i}+\epsilon_{2j}+\epsilon_{3l})/kT} \\ &= \sum_i \sum_j \sum_l e^{-\epsilon_{1i}/kT} \cdot e^{-\epsilon_{2j}/kT} \cdot e^{-\epsilon_{3l}/kT} \end{aligned} \qquad 7.36$$

Now, because the product $(x_1+x_2+x_3+\ldots)(y_1+y_2+y_3+\ldots)(z_1+z_2+z_3+\ldots)$ includes all combinations of the product $x_i y_j z_l$, it is possible to write

$$\sum_i x_i \sum_j y_j \sum_l z_l = \sum_i \sum_j \sum_l x_i\, y_j\, z_l$$

It follows that, since $\epsilon_{1i}$, $\epsilon_{2j}$ and $\epsilon_{3l}$ are independent, equation 7.36 may be written as

$$Z = \sum_i e^{-\epsilon_{1i}/kT} \sum_j e^{-\epsilon_{2j}/kT} \sum_l e^{-\epsilon_{3l}/kT} \qquad 7.37$$

If, therefore, three independent partition functions are defined as

$$Z_1 = \sum_i e^{-\epsilon_{1i}/kT}, \quad Z_2 = \sum_j e^{-\epsilon_{2j}/kT}, \quad Z_3 = \sum_l e^{-\epsilon_{3l}/kT}$$

then equation 7.37 can be written as the product

$$Z = Z_1 Z_2 Z_3 \qquad 7.38$$

* That is to say that, if two different states $i$ and $i'$ of one form of motion have the same value of energy so that $\epsilon_{1i'} = \epsilon_{1i}$, the terms $e^{-\epsilon_{1i}/kT}$ and $e^{-\epsilon_{1i'}/kT}$ must be counted independently in the partition function.

Now the mean energy of a system, for which the partition function is $Z$ and the temperature of the assembly is $T$, is given by $\bar{\epsilon}_t = kT^2\left\{\frac{\partial \log Z}{\partial T}\right\}_V$. Substitution from equation 7.38 thus gives

$$\bar{\epsilon}_t = kT^2\left\{\frac{\partial \log Z_1}{\partial T}+\frac{\partial \log Z_2}{\partial T}+\frac{\partial \log Z_3}{\partial T}\right\}_V \qquad 7.39$$

$$\equiv \bar{\epsilon}_1+\bar{\epsilon}_2+\bar{\epsilon}_3 \qquad 7.40$$

where $\bar{\epsilon}_1$, $\bar{\epsilon}_2$ and $\bar{\epsilon}_3$ may be taken as the mean energies corresponding to the three independent forms of the motion of a system. (This equation for the mean energy is, of course, of the form expected for a system having its energy made up of three *independent* components.)

It may be concluded that, for a system having more than one degree of freedom, it is possible for the partition function to be divided into its component parts. The complete treatment of the separation of such a partition function is given in section 8.3 for the case of a diatomic molecule. However, it is convenient to give a tentative discussion of the total partition function of a semi-classical perfect gas at this point. If a semi-classical perfect gas consisting of $N$ non-interacting molecules at temperature $T$ is considered as comprising a single, macroscopic system composed of molecular sub-systems, then the partition function of this macroscopic system may be written as a total partition function

$$\mathbf{Z} = \sum_{\text{all states}} e^{-(\epsilon_{1i}+\epsilon_{2j}+\epsilon_{3l}+\epsilon_{4m}+\ldots)/kT} \qquad 7.41$$

where $\epsilon_{1i}$, $\epsilon_{2j}$, etc., are the energies of the individual molecules, or sub-systems, 1, 2, etc., in the states $i$, $j$, etc., and the summation is taken over all allowed states or arrangements of the gas molecules. The partition function in equation 7.41 may be split into its component parts as was done in equation 7.37 to give

$$\mathbf{Z} = \frac{1}{N!}\sum_i e^{-\epsilon_{1i}/kT}\sum_j e^{-\epsilon_{2j}/kT}\sum_l e^{-\epsilon_{3l}/kT}\ldots \qquad 7.42$$

The division by $N!$ in equation 7.42 is necessary because, in the product of the summations, each term will in fact occur $N!$ times. (Consider three molecules labelled 1, 2 and 3 and let them be in the $i$th, $j$th and $l$th state respectively. If the molecules are indistinguishable, the rearrangement of the molecules among the three

states does not produce new, distinguishable states or arrangements. Thus the 3! arrangements of the energies $\epsilon_{1i}$, $\epsilon_{2j}$, $\epsilon_{3l}$ between the three molecules in the form:

$$\left.\begin{aligned}
&\epsilon_{1i}+\epsilon_{2j}+\epsilon_{3l}\\
&\epsilon_{1j}+\epsilon_{2i}+\epsilon_{3l}\\
&\epsilon_{1j}+\epsilon_{2l}+\epsilon_{3i}\\
&\epsilon_{1i}+\epsilon_{2l}+\epsilon_{3j}\\
&\epsilon_{1l}+\epsilon_{2j}+\epsilon_{3i}\\
&\epsilon_{1l}+\epsilon_{2i}+\epsilon_{3j}
\end{aligned}\right\} \text{3! equivalent indistinguishable arrangements}$$

are equivalent to a single arrangement. Extending this argument to the case of $N$ sub-systems it is seen that, because of the indistinguishability of the sub-systems, there are $N!$ times as many terms in the product of the summations in equation 7.42 as there are in the expression in 7.41.)

Because the molecules are indistinguishable the individual summation terms in equation 7.42 will be the same so that it is possible to write

$$\sum_i e^{-\epsilon_{1i}/kT} = \sum_j e^{-\epsilon_{2j}/kT} = \sum_l \ldots = \ldots = Z$$

being the partition function for each molecule. Equation 7.42 then gives the expression for the total partition function as

$$\mathbf{Z} = \frac{Z^N}{N!}$$

in agreement with equation 7.31.

The total partition function for the translational motion alone may be obtained using an integral form similar to that used in obtaining equation 7.15 except that the density of states will be replaced by $dp_x dp_y dp_z dx dy dz/h^3$. The single partition function for the molecule 1 is simply

$$\begin{aligned}
Z &= \sum_i e^{-\epsilon_{1i}/kT}\\
&\equiv \int_{\Gamma_1} e^{-\epsilon_1/kT} \frac{dp_{x1}dp_{y1}dp_{z1}dx_1dy_1dz_1}{h^3}
\end{aligned}$$

where $\Gamma_1$ represents the available volume of phase space and the coordinates $p_{x1}$ and $x_1$, etc., define the position of the sub-system

1 in its six-dimensional phase space. The total partition function in equation 7.42 is then

$$\begin{aligned} \mathbf{Z} &= \frac{1}{N!h^{3N}} \int_{\Gamma_1} e^{-\epsilon_1/kT}\, dp_{x1} dp_{y1} dp_{z1} dx_1 dy_1 dz_1 \\ &\quad \times \int_{\Gamma_2} e^{-\epsilon_2/kT}\, dp_{x2} dp_{y2} \ldots \int_{\Gamma_N} e^{-\epsilon_N/kT}\, dp_{xN} \ldots dz_N \\ &= \frac{1}{N!h^{3N}} \int_{\Gamma_{6N}} e^{-(\epsilon_1+\epsilon_2+\epsilon_3 \ldots +\epsilon_N)/kT} \\ &\quad \times dp_{x1} dp_{y1} dp_{z1} dx_1 dy_1 dz_1 \ldots \\ &\quad \ldots dp_{xN} dp_{yN} dp_{zN} dx_N dy_N dz_N \end{aligned} \qquad 7.43$$

where $\Gamma_{6N}$ represents the available volume of the $6N$-dimensional phase space for all the $N$ sub-systems. Since the total energy of the $N$ sub-systems is

$$E = \epsilon_1 + \epsilon_2 + \epsilon_3 + \ldots + \epsilon_N$$

equation 7.43 may be re-written as

$$\boxed{\mathbf{Z} = \frac{1}{N!h^{3N}} \int_{\Gamma_{6N}} e^{-E/kT}\, dp_{x1} \ldots dz_N} \qquad 7.44$$

In the case of a perfect gas of non-interacting molecules as considered here the energy is independent of the positions of the molecules. Therefore the integrals over the $3N$ spatial coordinates will simply give $[\int_V dxdydz]^N = V^N$ where $V$ is the volume occupied by the gas. The total partition function will then be

$$\begin{aligned} \mathbf{Z} &= \frac{V^N}{N!h^{3N}} \int_{-\infty}^{\infty} e^{-E/kT}\, dp_{x1} dp_{y1} dp_{z1} \ldots \\ &\quad \ldots dp_{xN} dp_{yN} dp_{zN} \end{aligned} \qquad 7.45$$

where the range of the momentum from $-\infty$ to $\infty$ applies to each momentum coordinate individually.

It must be remembered here that the derivation of equation 7.44 is based on the assumption that there are no interactions between the molecules. The extension of this equation to include interaction energies will be given in Chapter 9.

Finally it is noted that, for a molecule which is not structureless, there will be contributions to the total partition function due to

the different modes of motion. If, for example, these modes of motion give a partition function for each sub-system of the form $Z = Z_1 Z_2 Z_3$, as in equation 7.38, the total partition function will then be given by equation 7.31 for $N$ such sub-systems as

$$\mathbf{Z} = \frac{(Z_1 Z_2 Z_3)^N}{N!} \qquad 7.46$$

## PROBLEMS

1. Show that, when two different gases A and B of volume $V_A$ and $V_B$ and with $N_A$ and $N_B$ molecules respectively are mixed together at constant temperature to form a volume $V_A + V_B$, there is an increase in the total entropy given by the mixing term

$$k[(N_A + N_B)\log(V_A + V_B) - N_A \log V_A - N_B \log V_B]$$

Hence deduce that, when $V_A = V_B$ and $N_A = N_B = N$, the mixing term is $2Nk \log 2$.

2. Show that the Sackur–Tetrodé equation (7.29) may also be written as

$$S = Nk(\tfrac{5}{2}\log T - \log p + \tfrac{5}{2}\log k + \tfrac{3}{2}\log 2\pi m - 3\log h + \tfrac{5}{2})$$

where $p$ is the pressure of the perfect gas.

3. Derive the equation of state and the total energy of a semi-classical perfect gas from the expression for the free energy as given in equation 7.30. Explain why the results obtained are the same as for a classical perfect gas while the entropy obtained from this free energy is not.

4. By evaluating the integral

$$\int_{x=0}^{L}\int_{p_x=-\infty}^{\infty} e^{-p_x^2/2mkT}\frac{dx\,dp_x}{h} = Z_x$$

obtain a partial partition function for the translation of a system in one dimension with the motion limited to the region $0 \leqslant x \leqslant L$. Hence show that the partition function for translational motion in three dimensions as given in equation 7.28 is given by

$$Z = Z_x Z_y Z_z$$

and that the energy per degree of freedom calculated as $kT^2\{\partial \log Z_x/\partial T\}_L$ is $\frac{1}{2}kT$.

5. Show that the total partition function derived from equation 7.45, on the assumption that the energy of the $N$ sub-systems is

$$E = \frac{p_{x1}^2}{2m} + \frac{p_{y1}^2}{2m} + \frac{p_{z1}^2}{2m} + \ldots + \frac{p_{xN}^2}{2m} + \frac{p_{yN}^2}{2m} + \frac{p_{zN}^2}{2m}$$

agrees with that obtained by substituting equation 7.28 in equation 7.31, i.e.

$$\boxed{Z = \frac{V^N}{N!h^{3N}}(2\pi mkT)^{3N/2}} \qquad 7.47$$

6. Using equation 7.3 obtain a value for $\log W_{max}$ in terms of the energy $E$ and the number of systems $N$ only. (Use must be made of the values of $T$ and $\alpha$ given in Chapter 2.)

Chapter 8

# Applications of Statistical Thermodynamics

In this chapter consideration will be given to a few examples of the physical application of statistical thermodynamics. The methods given will not, in general, be the only ones by which the chosen problems could be treated and alternative methods are therefore indicated where this appears to be appropriate. Also, because the statistical method has been developed so far only for those assemblies having a fixed energy and a fixed number of systems, the applications considered do not, strictly, include any which involve interactions between the systems. However, because the properties of the assemblies have been considered in terms of the temperature rather than the energy, it will be seen later that the results are more general than would be the case for fixed energy assemblies.

## 8.1. *The paramagnetic gas*

Consider a gas in which each molecule has an intrinsic magnetic moment. When a magnetic field is applied to the gas there will be an induced paramagnetic moment per unit volume of the gas given by

$$m = \chi H \qquad 8.1$$

where $\chi$ is the paramagnetic susceptibility of the gas per unit volume and $H$ is the applied field. The form which is found for the paramagnetic susceptibility will depend on whether the magnetic moments are treated classically or quantum mechanically (although, as will be seen, the difference between the results in the two cases is slight). In order to illustrate this point both cases will be treated here even though the problem is only strictly amenable to a quantum mechanical treatment.

### THE CLASSICAL PARAMAGNETIC SUSCEPTIBILITY

Suppose that the gas contains $n$ molecules per unit volume, each molecule possessing an intrinsic magnetic moment $\mu$, and that

there is no interaction between the molecules. When a magnetic field is applied to the gas any molecule which has its magnetic moment pointing at an angle $\theta$ to the direction of the field will have a magnetic energy of

$$\epsilon(\theta) = -\mu H \cos\theta \qquad 8.2$$

compared with its magnetic energy when $\theta = \pi/2$. (The particular angular position of the magnetic moment which is taken as representing zero magnetic energy is unimportant since $\epsilon(\theta)$ is an energy of rotation, not of translation, and hence any constant terms in $\epsilon(\theta)$ will disappear from the subsequent analysis.)

The partition function for the magnetic energy of the molecules is given by

$$\begin{aligned} Z_{\text{mag}} &= \sum_{\theta} e^{-\epsilon(\theta)/kT} \\ &= \sum_{\theta} e^{+\mu H \cos\theta/kT} \end{aligned} \qquad 8.3$$

where the summations are over all possible values of the angles $\theta$. Let it now be assumed that the number of states available for molecules with their magnetic moments pointing at an angle $\theta$ within an element of solid angle $d\omega$ is proportional to the magnitude of $d\omega$. Equation 8.3 may then be replaced by an integral so that

$$Z_{\text{mag}} = \int_{\theta=0}^{\pi} e^{\mu H \cos\theta/kT} C\, d\omega \qquad 8.4$$

where $C$ is some constant of proportionality which it is not necessary to define here.

The solid angle which is included in the conical element between the direction $\theta$ and $\theta + d\theta$ is

$$d\omega = 2\pi \sin\theta\, d\theta$$

so that equation 8.4 can be written

$$\begin{aligned} Z_{\text{mag}} &= 2\pi C \int_{\theta=0}^{\pi} e^{\mu H \cos\theta/kT} \sin\theta\, d\theta \\ &= 2\pi C \cdot \frac{kT}{\mu H}\left[e^{\mu H/kT} - e^{-\mu H/kT}\right] \\ &= 4\pi C \cdot \frac{kT}{\mu H} \sinh\frac{\mu H}{kT} \end{aligned} \qquad 8.5$$

The magnetic energy of the $n$ molecules in unit volume of the gas is obtained using equation 7.11 in the form

$$E_{\text{mag}} = \frac{nkT^2}{Z_{\text{mag}}} \frac{\partial Z_{\text{mag}}}{\partial T}$$

which, on substitution from equation 8.5, becomes

$$E_{\text{mag}} = \frac{nkT}{\sinh \dfrac{\mu H}{kT}} \left\{ \sinh \frac{\mu H}{kT} - \frac{\mu H}{kT} \cosh \frac{\mu H}{kT} \right\}$$

$$= n\mu H \left\{ \frac{kT}{\mu H} - \coth \frac{\mu H}{kT} \right\} \qquad 8.6$$

If there is an induced magnetic moment $m$ per unit volume in the direction of the applied field then this magnetic energy may be expressed in a form similar to that of equation 8.2 so that

$$E_{\text{mag}} = -mH \qquad 8.7$$

Substitution from equation 8.6 now gives

$$m = -\frac{E_{\text{mag}}}{H}$$

$$= n\mu \left\{ \coth \frac{\mu H}{kT} - \frac{kT}{\mu H} \right\}$$

$$= n\mu L \left\{ \frac{\mu H}{kT} \right\} \qquad 8.8$$

where the Langevin function $L(x)$ is defined so that $L(x) = \coth x - 1/x$. When the condition $x \gg 1$ is satisfied then $L(x)$ will approximate to unity; thus at values of applied magnetic field such that $\mu H \gg kT$ equation 8.8 predicts that the induced magnetic moment will approach its maximum, or saturation, value $n\mu$. When, on the other hand, $x \ll 1$ then expansion of $L(x)$ to terms involving $x^3$ gives the approximation

$$L(x) \simeq \frac{x}{3}$$

In this case equation 8.8 gives the magnetic moment as

$$m = \frac{n\mu^2}{3kT} H \qquad 8.9$$

The corresponding behaviour of the Langevin function is illustrated in Fig. 22.

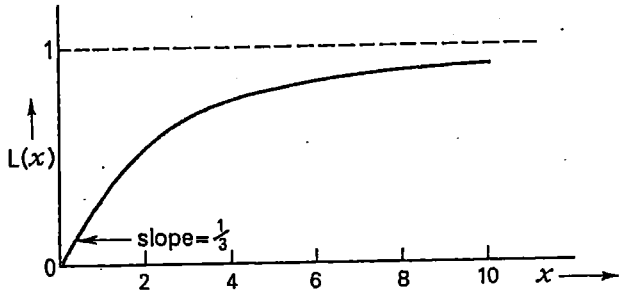


Fig. 22. The Langevin function $L(x) = \coth x - \frac{1}{x}$.

From equation 8.9 the paramagnetic susceptibility, defined in equation 8.1 by the relationship $\chi = m/H$, is given as

$$\chi = \frac{n\mu^2}{3kT} \qquad 8.10$$

for the low field case.

(It is left as an exercise for the student to show that the same results for $m$ and $\chi$ are obtained if the value of the total magnetic moment along the direction of the magnetic field is taken to be the sum of all the components $\mu \cos\theta$ of the individual moments of the molecules. This is equivalent to evaluating the average moment in a manner similar to that indicated in equation 3.4, i.e.

$$\bar{\mu} = \frac{\int_0^\pi \mu \cos\theta \, e^{\mu H \cos\theta/kT} C \, d\omega}{\int_0^\pi e^{\mu H \cos\theta/kT} C \, d\omega}$$

where $C$ and $d\omega$ have already been given and $e^{\mu H \cos\theta/kT}$ is the Boltzmann factor $e^{-\epsilon/kT}$. The induced magnetic moment per unit volume is then $m = n\bar{\mu}$.)

## THE QUANTUM MECHANICAL PARAMAGNETIC SUSCEPTIBILITY

In quantum mechanics the angular momentum of an atom or molecule is defined by the total angular momentum quantum number $J$ which is, of course, an integer. The magnetic quantum number $M_J$, the component of $J$ along the direction of an applied magnetic field, can take only the allowed integral values

$$M_J = J, J-1, J-2, \ldots, 0, \ldots -(J-1), -J$$

For a molecule with a given value of $M_J$ the component of its magnetic moment along the direction of the applied magnetic field is given by

$$\mu_H = g\mu_B M_J \tag{8.11}$$

where $\mu_B$ is the Bohr magneton and $g$ is the spectroscopic (or Landé) splitting factor of the molecule. Taking the magnetic potential energy of the molecule as $-\mu_H H$ in agreement with equation 8.2 the partition function for the molecule becomes

$$\begin{aligned} Z_{\text{mag}} &= \sum_{M_J=-J}^{M_J=+J} e^{\mu_H H/kT} \\ &= \sum_{M_J=-J}^{M_J=+J} e^{g\mu_B M_J H/kT} \end{aligned} \tag{8.12}$$

Again it is convenient to evaluate this partition function in the two limiting cases where $H$ is either very large or very small. When $H$ is very large the term in which $M_J = J$ will be very much larger than any of the others. This will correspond to the case where all the magnetic moments are aligned along the direction of the applied field to give the maximum possible magnetic moment $ng\mu_B J$.

In the low field region the approximation $e^x \simeq 1+x+\frac{1}{2}x^2$ may be used in equation 8.12 to give

$$\begin{aligned} Z_{\text{mag}} &\simeq \sum_{M_J=-J}^{M_J=+J} \left[1+\left\{\frac{g\mu_B H}{kT}\right\}M_J+\tfrac{1}{2}\left\{\frac{g\mu_B H}{kT}\right\}^2 M_J^2\right] \\ &= (2J+1)+\left\{\frac{g\mu_B H}{kT}\right\}^2 \frac{J(J+1)(2J+1)}{6} \end{aligned} \tag{8.13}$$

Substituting once again in equation 7.11, the total magnetic energy for a gas with $n$ such molecules per unit volume becomes

$$\begin{aligned} E_{\text{mag}} &= nkT^2 \frac{\partial}{\partial T} \log\left[(2J+1)\right. \\ &\qquad \left. +\left\{\frac{g\mu_B H}{kT}\right\}^2 \frac{J(J+1)(2J+1)}{6}\right] \\ &= -\frac{n}{kT} \frac{(g\mu_B H)^2 \dfrac{J(J+1)(2J+1)}{3}}{(2J+1)+\left\{\dfrac{g\mu_B H}{kT}\right\}^2 \dfrac{J(J+1)(2J+1)}{6}} \end{aligned} \tag{8.14}$$

In the low field limit where $g\mu_B H \ll kT$ the denominator of equation 8.14 is very nearly $2J+1$ and therefore

$$E_{mag} \simeq -\frac{ng^2\mu_B^2 J(J+1)}{3kT}H^2 \qquad 8.15$$

This energy again corresponds to a magnetic moment per unit volume of $-E_{mag}/H$ so that

$$m = \frac{ng^2\mu_B^2 J(J+1)}{3kT}H \qquad 8.16$$

The corresponding susceptibility per unit volume, $m/H$, is

$$\chi = \frac{ng^2\mu_B^2 J(J+1)}{3kT} \qquad 8.17$$

A comparison of equation 8.17 with the paramagnetic susceptibility given by equation 8.10 shows that the quantum mechanical molecule behaves, in this approximation, as a classical molecule with an effective magnetic moment

$$\mu = g\mu_B\sqrt{\{J(J+1)\}}$$

(Again it is left as an exercise for the student to show that the same results are obtained by finding the average moment of the molecules in the direction of the field from the relationship

$$\bar{\mu}_H = \frac{\sum_{M_J=-J}^{M_J=+J} g\mu_B M_J\, e^{g\mu_B M_J H/kT}}{\sum_{M_J=-J}^{M_J=+J} e^{g\mu_B M_J H/kT}}$$

and taking $m = n\bar{\mu}_H$.)

## 8.2. *The harmonic oscillator*

According to classical mechanics there is no restriction on the energy of a simple harmonic oscillator. It follows therefore that, as shown in section 3.6, the mean energy of a classical one-dimensional harmonic oscillator in an assembly at temperature $T$ is $kT$. On the other hand if the one-dimensional harmonic oscillator obeys quantum mechanics it may only have an energy given by one of the discrete values

$$\epsilon = (n+\tfrac{1}{2})h\nu \qquad 8.18$$

where $\nu$ is the oscillator frequency and $n$ is a positive integer. The lowest energy available to such a quantum mechanical oscillator is $\frac{1}{2}h\nu$ and is known as the *zero point energy.*

The mean energy of a quantum mechanical harmonic oscillator at a temperature $T$ can be found by setting up the partition function as

$$Z = \sum_{n=0}^{\infty} e^{-(n+\frac{1}{2})h\nu/kT}$$

$$= e^{-\frac{1}{2}h\nu/kT} \sum_{n=0}^{\infty} e^{-nh\nu/kT} \qquad 8.19$$

The summation term in equation 8.19 is equivalent to the summation $\sum_{n=0}^{\infty} x^n = (1-x)^{-1}$ so that the partition function is

$$\boxed{Z = \frac{e^{-\frac{1}{2}h\nu/kT}}{(1-e^{-h\nu/kT})}} \qquad 8.20$$

The mean energy of the oscillator, as given by $\bar{\epsilon} = kT^2\left\{\frac{\partial \log Z}{\partial T}\right\}_\nu$, is thus

$$\boxed{\bar{\epsilon} = h\nu\left\{\tfrac{1}{2} + \frac{1}{e^{h\nu/kT}-1}\right\}} \qquad 8.21$$

(At high temperatures where $h\nu/kT \ll 1$ it is possible to substitute in equation 8.21 for

$$e^{h\nu/kT} \simeq 1 + \left\{\frac{h\nu}{kT}\right\} + \tfrac{1}{2}\left\{\frac{h\nu}{kT}\right\}^2$$

with the higher order terms neglected. The mean energy of the oscillator is then

$$\bar{\epsilon} \simeq h\nu\left\{\tfrac{1}{2} + \frac{1}{\frac{h\nu}{kT} + \frac{1}{2}\left(\frac{h\nu}{kT}\right)^2}\right\}$$

$$\simeq h\nu\left\{\tfrac{1}{2} + \frac{kT}{h\nu}\left(1 - \tfrac{1}{2}\frac{h\nu}{kT}\right)\right\}$$

$$= kT$$

as is expected for the high temperature limit where the distinction between classical and quantum systems is not important.)

By treating the atoms in a solid as simple harmonic oscillators with their mean energies given by equation 8.21 it is possible to calculate the specific heat of the solid. Such a calculation would involve the assumption of a distribution of the oscillator frequencies in a manner such as that of Debye which is described in section 4.4. While the result obtained on the basis of this assumption may be seen by inspection to be the same as the Debye specific heat of section 4.4, it is left as an exercise for the student to calculate the specific heat obtained from Einstein's assumption of a single oscillator frequency (see problem 8).

## 8.3. *The diatomic molecule*

In a diatomic molecule the energy may be considered as being made up of five independent contributions. These contributions are due to:

the translational and rotational motion of the molecule as a whole,
the vibrational motion of the two atoms along the axis of the molecule,
the motion of the electrons around the nuclei,
the nuclear spin.

The energy levels which are available for these five forms of motion are necessarily quantized and only in the case of the translational motion is it possible to treat these levels as an approximate classical continuum. In the other cases the energy levels must be treated as completely discrete except, perhaps, at very high temperatures.

In order to study the thermodynamic properties of the perfect diatomic gas it is necessary to establish the partition function of a molecule in the gas in terms of the separate partition functions for the different forms of motion. Following the method outlined in section 7.6 it is possible to factorize the partition function so that

$$Z = Z_t Z_r Z_v Z_e Z_n \qquad 8.22$$

where $Z_t$ is the translational partition function,
$Z_r$ „ „ rotational „ „ ,
$Z_v$ „ „ vibrational „ „ ,
$Z_e$ „ „ electronic „ „ ,
and $Z_n$ „ „ nuclear spin „ „ .

Since the nuclear spin partition function generally involves only multiplication by a constant factor, discussion of this term will be given later in the section after values have been determined for the other components.

The translational motion of the diatomic molecule is quite analogous to that already considered for a structureless molecule and the partition function $Z_t$ will therefore be equal to that given in equation 7.28, i.e.

$$Z_t = \frac{V}{h^3}(2\pi mkT)^{\frac{3}{2}} \tag{7.28}$$

In the determination of the rotational partition function of the diatomic molecule it is necessary to write the allowed rotational energy levels $\epsilon_j$ in the quantum mechanical form*

$$\epsilon_j = j(j+1)\frac{h^2}{8\pi^2\mathscr{I}} \tag{8.23}$$

where $j$, the total angular momentum quantum number of the rotational motion, is a positive integer and $\mathscr{I}$ is the moment of inertia of the molecule about an axis through its centre of gravity and normal to the line joining the two atoms. For each value of the quantum number $j$ the magnetic quantum number $m_j$ may take any of the integral values between $j$ and $-j$, i.e. any one of $(2j+1)$ values. Each energy level $\epsilon_j$ thus represents $(2j+1)$ states and, allowing for this degeneracy, the rotational partition function becomes

$$\begin{aligned} Z_r &= \sum_{j=0}^{\infty} (2j+1)\, e^{-\epsilon_j/kT} \\ &= \sum_{j=0}^{\infty} (2j+1)\, e^{-j(j+1)K/kT} \end{aligned} \tag{8.24}$$

where $K = h^2/8\pi^2\mathscr{I}$.

The vibrational motion of the molecule may be assumed, to good approximation, to be simple harmonic in form and to be sensibly free from any anharmonic distortions. It is possible, therefore, to take the vibrational partition function of the molecule as that given in equation 8.20 for the one-dimensional simple

* A proof of this equation 8.23 is given, for example, in Glasstone, S.: *Theoretical Chemistry*, D. Van Nostrand Co. Inc. 1947.

harmonic oscillator; i.e.

$$Z_v = \frac{e^{-\frac{1}{2}h\nu/kT}}{1-e^{-h\nu/kT}} \tag{8.20}$$

where $\nu$, the characteristic frequency of the molecular vibrations, is determined by the mass of the atoms making up the molecule and the nature of the coupling between them.

The electronic partition function can usually be represented with sufficient accuracy by the first two energy terms in the normal summation. If the energies required to excite an electron from the ground state to the first, second, etc., excited states of the molecule are $\epsilon_{e1}$, $\epsilon_{e2}$, etc., then the partition function will be effectively,

$$Z_e = g_0 + g_1 e^{-\epsilon_{e1}/kT} + g_2 e^{-\epsilon_{e2}/kT} + \ldots \tag{8.25}$$

where $g_0$ is the degeneracy of the ground state and $g_1$, $g_2$, etc., are the degeneracies of the respective excited states. The energies $\epsilon_{e1}$ and $\epsilon_{e2}$ are, in general, very much larger than the thermal energy $kT$ except in the case of very high temperatures as will be discussed below. It is generally possible, therefore, to replace equation 8.25 by

$$Z_e \simeq g_0 + g_1 e^{-\epsilon_{e1}/kT} \tag{8.26}$$

The complete partition function of a diatomic molecule is thus obtained from its component parts, as indicated in equation 8.22, as

$$Z = \frac{V}{h^3}(2\pi mkT)^{\frac{3}{2}}\left\{\sum_{j=0}^{\infty}(2j+1)\,e^{-j(j+1)K/kT}\right\}\left\{\frac{e^{-\frac{1}{2}h\nu/kT}}{1-e^{-h\nu/kT}}\right\}$$
$$\times\{g_0 + g_1 e^{-\epsilon_{e1}/kT}\}Z_n \tag{8.27}$$

The total partition function of a gas of $N$ identical molecules will then follow from equation 7.31 as $Z^N/N!$.

Following the method used in the derivation of equation 7.38 the energy of the gas of $N$ diatomic molecules may be written as

$$E = NkT^2\left[\frac{\partial \log Z_t}{\partial T} + \frac{\partial \log Z_r}{\partial T} + \frac{\partial \log Z_v}{\partial T} + \frac{\partial \log Z_e}{\partial T}\right]$$
$$= N\left\{\tfrac{3}{2}kT + kT^2\frac{\partial}{\partial T}\log\left[\sum_{j=0}^{\infty}(2j+1)\,e^{-j(j+1)K/kT}\right]\right.$$
$$\left. + h\nu\left(\tfrac{1}{2} + \frac{1}{e^{h\nu/kT}-1}\right) + \frac{g_1\epsilon_{e1}\,e^{-\epsilon_{e1}/kT}}{g_0 + g_1 e^{-\epsilon_{e1}/kT}}\right\} \tag{8.28}$$

and there is no contribution from the term $Z_n$ which is taken to be temperature independent.

So that the magnitudes of the various contributions to the energy $E$ in equation 8.28 may be more readily appreciated it is convenient to define characteristic temperatures for the rotation, vibration and electronic energies. As will be appreciated from the subsequent discussion these temperatures are most conveniently taken as $\theta_{rot} = K/k = h^2/8\pi^2\mathscr{I}k$; $\theta_{vib} = h\nu/k$ and $\theta_e = \epsilon_{e1}/k$. The magnitudes of these characteristic temperatures may be found from the properties of the molecules and in general they are found to satisfy the inequalities $\theta_{rot} \ll \theta_{vib} \ll \theta_e$. For example, in the case of the hydrogen molecule their values are:

$$\theta_{rot} = 85{\cdot}5°\text{K}; \quad \theta_{vib} = 6140°\text{K}; \quad \theta_e = 118{,}000°\text{K}$$

For other diatomic molecules the characteristic temperatures have a similar relationship to those for the hydrogen molecule but are, in general, rather lower. Thus, for the chlorine molecule, $\theta_{rot} = 0{\cdot}35°\text{K}, \theta_{vib} = 810°\text{K}$ and $\theta_e = 25{,}500°\text{K}$.

At low temperatures where $T \ll \theta_{rot}$ it is clear from the forms of the partition functions that only an insignificant fraction of the molecules will be in rotation, vibration or electronic energy levels above the ground state. In this case the total energy of the molecules will be due to their translational motion together with the zero point energy of the vibrational motion, i.e. $\frac{1}{2}Nh\nu$, and the ground state energy of the electrons. Of these three terms only the translational energy, given by equation 8.28 as $\frac{3}{2}NkT$, will be dependent on the temperature so that, for $T \ll \theta_{rot}$, the specific heat of the gas at constant volume will be

$$C_v = \left\{\frac{\partial E}{\partial T}\right\}_V = \tfrac{3}{2}Nk \qquad 8.29$$

(At these low temperatures the components of the partition function given in equation 8.27 may be taken as $Z_t = V/h^3(2\pi mkT)^{\frac{3}{2}}$, $Z_r \simeq 1$, $Z_v \simeq e^{-\frac{1}{2}h\nu/kT}$, $Z_e \simeq g_0$ while $Z_n$ is again a constant.)

If the temperature is increased until it is of the order of $\theta_{rot}$ some of the molecules will be excited to take up rotational energy states above the ground state. The rotational motion will then contribute to both the total energy and the specific heat of the gas while the vibrational motion will still be in its ground state. In

the case where the temperature is further increased to values $T \gg \theta_{rot}$ it is possible to obtain an approximate value for the rotational partition function $Z_r$ by replacing the summation in equation 8.24 by an integration over the variable $j$. Then, since $\theta_{rot}/T \ll 1$, in this case

$$Z_r = \sum_{j=0}^{\infty} (2j+1)\, e^{-j(j+1)\theta_{rot}/T}$$

becomes

$$\begin{aligned} Z_r &= \int_0^{\infty} (2j+1)\, e^{-j(j+1)\theta_{rot}/T}\, dj \\ &= e^{\theta_{rot}/4T} \int_0^{\infty} e^{-(j+\frac{1}{2})^2\theta_{rot}/T} 2(j+\tfrac{1}{2})\, d(j+\tfrac{1}{2}) \\ &= e^{\theta_{rot}/4T} \frac{T}{\theta_{rot}} \end{aligned}$$

or, with $e^{\theta_{rot}/4T} \simeq 1$ in this approximation,

$$Z_r \simeq \frac{T}{\theta_{rot}} \qquad 8.30$$

The rotational energy at these temperatures is obtained as

$$\begin{aligned} E_r &= NkT^2 \frac{\partial \log Z_r}{\partial T} \\ &= NkT \end{aligned} \qquad 8.31$$

which corresponds to a classical energy of $\frac{1}{2}kT$ for each of the two classical degrees of freedom for the rotation of the molecules. The contribution to the specific heat of the gas at constant volume, obtained by differentiation of equation 8.31, is

$$C_{vr} = Nk \qquad 8.32$$

The vibrational energy levels of the molecules will not contribute to the temperature dependent part of the energy or to the specific heat of the gas until the temperature approaches the characteristic temperature $\theta_{vib}$. However, for high temperatures $T \gg \theta_{vib}$, the average vibrational energy will of course approach the classical value of $kT$ per molecule as shown in section 8.2. Thus the vibrational energy of the gas will approach the value

$$E_v = NkT \qquad 8.33$$

and the vibrational contribution to the specific heat in the temperature region $T \gg \theta_{vib}$ is then

$$C_{vv} = Nk \qquad 8.34$$

The total temperature dependent energy of the gas at high temperatures (for which $\theta_{rot} \ll \theta_{vib} \ll T \ll \theta_e$) is given by combining the translational, rotational and vibrational energy contributions of equations 8.29, 8.32 and 8.34 as

$$E = \tfrac{7}{2}NkT \qquad 8.35$$

and the corresponding total specific heat is

$$C_v = \tfrac{7}{2}Nk \qquad 8.36$$

This high temperature specific heat will be approached in a series of 'steps' as the temperature rises and will have a form similar to that shown in Fig. 23 where $Nk$ has been replaced by the gas constant $R$.

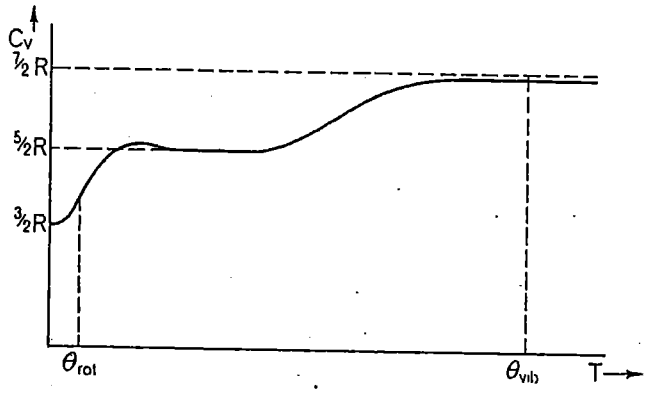


Fig. 23. The specific heat of a diatomic gas as a function of temperature.

The derivation of the specific heat given so far has neglected any possible contribution from the electronic energy levels. This implies that for all the diatomic molecules the condition $T \ll \theta_e$ is satisfied except at the very highest temperatures. For example, in oxygen the value of $\theta_e$ is about 11,000°K and this is one of the lowest values of $\theta_e$ for diatomic molecules. It follows that, in a gas composed of oxygen molecules, there will be no significant specific heat contribution from the electronic energy levels until the temperature of the gas is increased substantially above 2000°K. In this case the contribution of the electronic states to the partition function will thus be given, to sufficient approximation, by the

simple multiplicative factor $g_0$, the weight of the ground state. On the other hand the molecules of nitric oxide (NO) have a value of $\theta_e$ which is much smaller than for the oxygen molecule and the electronic energy levels give a contribution to the specific heat for temperatures in the neighbourhood of 80°K. This case is, however, an unusual one.

The variation of the specific heat which would be expected for a two energy level system, such as that discussed for the electronic energy states in the partition function of equation 8.26, will be considered in some detail in the next section.

The contribution of the nuclear spin to the partition function will arise, in general, from the degeneracy of the nuclear spin state. If the total spin contributed by the two nuclei of the molecule has the quantum number $I$ then this spin state will be $(2I+1)$-fold degenerate. These $(2I+1)$ states of very nearly the same energy correspond to the allowed values which may be taken by the magnetic quantum number $m_I$, i.e. $I, (I-1), \ldots, 0, \ldots, -(I-1), -I$. The partition function $Z_n$ may thus be replaced by the ground state term $(2I+1)$.

When the complete partition function is written, with the electronic and nuclear degeneracy terms included, it then becomes

$$Z = Z_t Z_r Z_v g_0(2I+1) \qquad 8.37$$

The temperature independent term $g_0(2I+1)$ results in a contribution $Nk\log[g_0(2I+1)]$ to the entropy of the gas but does not contribute to either the temperature dependent energy or the specific heat of the gas.

### HOMONUCLEAR MOLECULES

The discussion of the effect of the nuclear spin which has been given so far will only apply to the case of molecules in which the two nuclei are of different species (i.e. heteronuclear molecules). In the case of a diatomic molecule in which the two nuclei are identical (i.e. a homonuclear molecule) the state of the nuclear spin will determine the allowed rotational wave functions of the molecule because of the natural symmetry of the molecule. For example, for a hydrogen molecule (in which both nuclei are single protons) the total nuclear spin quantum number may be either $I = 0$ or $I = 1$. The allowed rotational wave functions are then such that $j$, the total angular momentum quantum number of the rotation of the molecule, must be even for $I = 0$ (para-hydrogen) and odd

for $I = 1$ (ortho-hydrogen). The total rotational partition function of the hydrogen molecule will thus be a combination of the rotational partition functions, $Z_{ro}$ and $Z_{rp}$, for ortho- and para-hydrogen respectively. Now, because the nuclear partition function is different for the two cases, the contribution to the total partition function due to the term $Z_r Z_n$ must be replaced by

$$Z_{no}Z_{ro} + Z_{np}Z_{rp}$$

where, using equation 8.24 with $K/k = \theta_{rot}$,

$$Z_{ro} = \sum_{j\,\text{odd}} (2j+1)\, e^{-j(j+1)\theta_{rot}/T}$$

and

$$Z_{rp} = \sum_{j\,\text{even}} (2j+1)\, e^{-j(j+1)\theta_{rot}/T}$$

Also, since $Z_n = (2I+1)$, then $Z_{no} = 3$ for $I = 1$ (the triplet state) and $Z_{np} = 1$ for $I = 0$ (the singlet state).

The actual numbers of molecules in the ortho- and para-states will depend on the magnitudes of the various terms in the partition function summations. At $T = 0°K$, the only state which will be occupied is that for which $j = 0$ since this has the lowest energy. Therefore, in the equilibrium state at this temperature, all the molecules will be in the form of para-hydrogen with $I = 0$. However, as the temperature is lowered towards absolute zero from some higher value, a considerable period may be required for the final equilibrium state to be established in view of the substantial relaxation time required for the nuclei to change from the $I = 1$ state to the $I = 0$ state.

Alternatively, at high temperatures where the summations over odd and even $j$-values are the same, there will be a 3 to 1 mixture of the ortho- and para-hydrogen respectively.

(If it is desired to treat more complex molecules than the simple diatomic molecule which has been considered here then, not only must allowance be made for a greater number of degrees of freedom for the rotational and vibrational motions, but also more complicated motions of the molecules, such as 'wagging' and 'rocking', need to be taken into account. Also it becomes necessary to allow for the fact that the rotational and vibrational motions can no longer be treated as being entirely independent.)

## 8.4. *The two energy level system*

Following the discussion which was given in the previous section on the effect of the electronic energy levels in a diatomic molecule, more detailed consideration will be given here to the case of a system for which there are two available energy levels.

Consider an assembly of $N$ systems, localized in space, each of which may be in one of two non-degenerate energy levels $\epsilon_2$ and $\epsilon_1$ where $\epsilon_2$, 'the excited state', is greater than $\epsilon_1$. As an alternative to the partition function method which has been used in the previous sections of this chapter, the equilibrium distribution of this assembly will be calculated by determining the condition for the free energy $F$ to be a minimum.

As the first step it is required to determine the entropy of the assembly when it is in a given configuration by applying the relation $S = k \log W$. Let there be $n$ systems in the upper energy state, $\epsilon_2$, and $(N-n)$ systems in the lower energy state, $\epsilon_1$, as shown in Fig. 24. The number of ways in which the configuration of Fig. 24

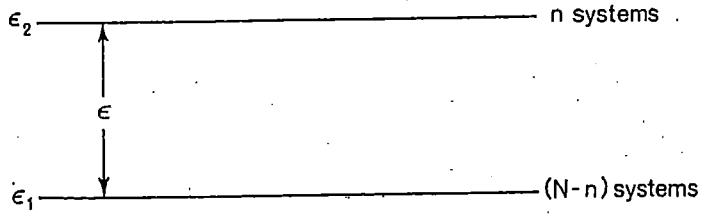


Fig. 24. Distribution of the systems among the two energy levels.

may be formed is*

$$W = \frac{N!}{n!\,(N-n)!} \qquad 8.38$$

if the localized systems are considered to be completely distinguishable. The entropy of the assembly in the configuration of Fig. 24 is then given by

$$S = k \log W$$
$$= k \log \frac{N!}{n!\,(N-n)!}$$

* For the upper state the $n$ systems may be chosen in ${}_NC_n = \dfrac{N!}{n!\,(N-n)!}$ and then the remaining $(N-n)$ systems of the lower state may only be chosen in one way.

which becomes, on using Stirling's approximation,

$$S = k[N \log N - n \log n - (N-n) \log(N-n)] \qquad 8.39$$

The free energy of the assembly is therefore

$$\begin{aligned} F &= E - TS \\ &= n\epsilon_2 + (N-n)\epsilon_1 - kT[N \log N - n \log n - \\ &\quad - (N-n) \log(N-n)] \end{aligned} \qquad 8.40$$

For the assembly to be in the equilibrium configuration at temperature $T$ the number of excited systems, $n$, will be such that this free energy is a minimum. That is

$$\frac{\partial F}{\partial n} = 0$$

Applying this condition to equation 8.40 gives

$$(\epsilon_2 - \epsilon_1) - kT[\log(N-n) - \log n] = 0$$

or

$$\frac{N-n}{n} = e^{(\epsilon_2 - \epsilon_1)/kT} \qquad 8.41$$

as would be expected if the ratio of the numbers of systems in the two states were obtained simply from the application of the Boltzmann factor. (It is left as an exercise for the student to show that equation 8.41 indeed represents the condition for a minimum of the free energy rather than a maximum.)

The number of systems in the upper energy level is obtained from equation 8.41 as

$$\begin{aligned} n &= \frac{N}{1 + e^{(\epsilon_2 - \epsilon_1)/kT}} \\ &= \frac{N}{1 + e^{\epsilon/kT}} \end{aligned} \qquad 8.42$$

where $\epsilon = \epsilon_2 - \epsilon_1$ is the energy gap between the two levels.

The total energy of the assembly is then simply

$$\begin{aligned} E &= n\epsilon_2 + (N-n)\epsilon_1 \\ &= N\epsilon_1 + \frac{N\epsilon}{1 + e^{\epsilon/kT}} \end{aligned} \qquad 8.43$$

The specific heat obtained from equation 8.43 with the volume, and hence the energy levels, maintained constant is

$$C_v = \left\{\frac{\partial E}{\partial T}\right\}_V$$

$$= \frac{N\epsilon^2}{kT^2}\frac{e^{\epsilon/kT}}{(1+e^{\epsilon/kT})^2} \qquad 8.44$$

or

$$C_v = Nk\left\{\frac{\theta}{T}\right\}^2 \frac{e^{\theta/T}}{(1+e^{\theta/T})^2} \qquad 8.45$$

where $\theta = \epsilon/k = (\epsilon_2 - \epsilon_1)/k$ is the characteristic temperature of the assembly. In Fig. 25 this specific heat is plotted as a function of $\theta/T$. It will be seen that there is a maximum value of $C_v \simeq 0{\cdot}45Nk$ for $\theta/T \simeq 2{\cdot}5$ while $C_v$ is clearly zero for both $T = 0$ and $T = \infty$.

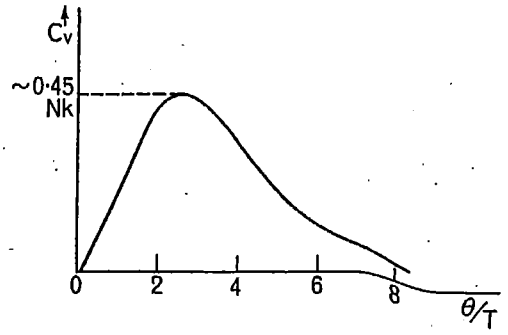


Fig. 25. Variation of the specific heat of an assembly of systems having two energy levels.

The variation of the entropy of the assembly may be considered in terms of the Boltzmann or Planck expressions which are here equivalent. It is clear that, when the assembly is ordered with all the systems in the ground state, the entropy will be zero. This follows from the fact that there is only one way of arranging such an ordered configuration, so that $W = 1$ and $\log W = 0$. This ordered condition will correspond to the case where the temperature $T$ in equation 8.42 is zero. As the temperature rises above the absolute zero the disorder and the entropy will increase as the number of excited systems, $n$, increases. If the temperature could tend to infinity then, according to equation 8.42, the

number of excited systems, $n$, would tend to a value $\frac{1}{2}N$ and the entropy, as given by equation 8.39, would have its maximum value

$$S_{\max} = Nk \log 2 \qquad 8.46$$

If it were possible to excite all the systems to the upper energy state so that $n = N$ the assembly would again be completely ordered and in a state of zero entropy. According to equation 8.42 this ordered situation could only be achieved if the temperature $T$ approached a value of zero from the negative temperature side. (That is, $1/\{1+e^{\epsilon/k(-T)}\} \to 0$ as $T \to 0$.) While a negative temperature of this magnitude is not obtainable in practice, it is possible to obtain finite negative temperatures as defined by equation 8.42. The mechanisms for producing such negative temperatures would be similar to those used in lasers for exciting the systems so that there are more in the upper energy state than in the lower. When this occurs the populations in the two states are said to be 'inverted' and, under this condition, it is necessary to ascribe a negative temperature to the particular aspect of the assembly under consideration. However, such a condition of the assembly is not an equilibrium condition and is therefore outside the general scope of this book.

(It is left as an exercise for the student to show that the results obtained here for the entropy and energy are also obtainable by the partition function method.)

## 8.5. *The disordered lattice*

As a final application of statistical thermodynamics in this chapter consideration will be given to the thermal disorder which may occur in a crystal lattice. One way in which this disorder may arise is through the displacement of atoms from their normal positions to interstitial positions by the thermal vibrations in the lattice. Suppose that in Fig. 26 the circles represent the normal positions of the atoms in a monatomic cubic lattice and that the crosses represent the possible interstitial positions which the atoms may occupy. If there are $N$ normal lattice points in the volume considered there will also be $N$ interstitial positions.

Let the energy required to remove an atom from a normal position to an interstitial position be $\epsilon$. Then, if there are $n$ such interstitial atoms, the energy of the lattice will be $n\epsilon$ above its ordered ground state. The number of ways of arranging these $n$

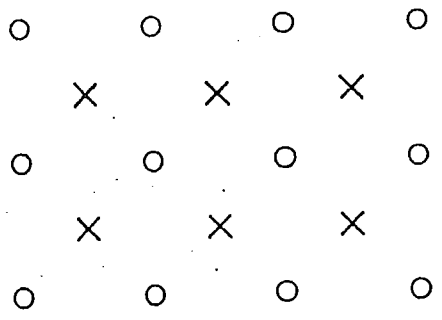

Fig. 26. Normal (○) and interstitial (×) positions in a lattice.

atoms among the $N$ localized, interstitial positions is ${}_NC_n = N!/\{n!\,(N-n)!\}$ while the number of ways of arranging the $(N-n)$ remaining atoms among the $N$ normal positions is also ${}_NC_n$. The weight of the configuration in which there are $n$ interstitial atoms is thus the product of these numbers so that

$$W = \left\{\frac{N!}{n!\,(N-n)!}\right\}^2$$

and the entropy arising from the displacement of the atoms is

$$S = k \log W$$

$$= k \log\left\{\frac{N!}{n!\,(N-n)!}\right\}^2$$

or, using Stirling's approximation,

$$S \simeq 2k[N \log N - n \log n - (N-n)\log(N-n)]$$

The corresponding free energy of the lattice, measured from the ground state, is

$$F = n\epsilon - 2kT[N \log N - n \log n - (N-n)\log(N-n)]$$

The condition for equilibrium, $\partial F/\partial n = 0$, becomes

$$\epsilon - 2kT[\log(N-n) - \log n] = 0$$

so that

$$n = \frac{N}{1+e^{\epsilon/2kT}} \qquad 8.47$$

## PROBLEMS

1. Show that at normal temperatures the entropy of a diatomic gas is, approximately,

$$S = Nk(\log V + \tfrac{3}{2}\log(2\pi mkT) - 3\log h + \log\left\{\sum_{j=0}^{\infty}(2j+1)\,e^{-j(j+1)\theta_{\mathrm{rot}}/T}\right\} + \log\left\{\frac{e^{-\theta_{\mathrm{vib}}/T}}{1-e^{-\theta_{\mathrm{vib}}/T}}\right\} + \log g_0 + \log(2I+1) + \tfrac{7}{2} - \log N)$$

2. Two different groups of $n$ fermions are distributed among $m$ states of the same energy where $m > n$. Show that the entropy is

$$2k[m\log m - n\log n - (m-n)\log(m-n)].$$

3. Show that, at high temperatures, the free energy of an assembly of quantum mechanical, one-dimensional oscillators approximates to $kT\log(h\nu/kT)$ per oscillator, corresponding to a mean energy of $kT$.

4. Evaluate the partition function at temperature $T$ for a classical one-dimensional oscillator having an energy

$$\epsilon = \frac{p_x^2}{2m} + \tfrac{1}{2}\mu x^2$$

and hence find the mean energy of such an oscillator at this temperature.

5. Show that the equation of state of a diatomic gas as derived from the partition function of equation 8.27 is the same as for a monatomic gas.

6. Calculate the maximum specific heat for an assembly of systems having two energy levels separated by an energy $\nu$ if the upper level is doubly degenerate.

7. Write out the partition function for a three-dimensional harmonic oscillator assuming that it obeys (*a*) classical, (*b*) quantum mechanics. Show that both give a mean energy of $3kT$ at high temperatures.

8. As a basis for the calculation of the specific heat of a solid, Einstein assumed that the $N$ atoms in the solid could be considered as forming $3N$ harmonic oscillators each with the same frequency $\nu$. Show that the specific heat of the solid in this case would be

$$C_v = 3R\left\{\frac{\theta_E}{T}\right\}^2 \frac{e^{\theta_E/T}}{[e^{\theta_E/T}-1]^2}$$

where $\theta_E = h\nu/k$ is known as the Einstein temperature and the mean oscillator energy is taken from section 8.2.

Chapter 9

# The Canonical Ensemble

## 9.1. *Ensembles*

Up to this point the discussion has been mainly limited to those assemblies in which both the total energy and the number of systems could be considered as fixed quantities and in which there were no interactions between the component systems. However, while it has been shown that the study of assemblies which satisfy these conditions can lead to useful results over a wide range of physical problems, the limitations imposed on the assemblies will also limit the range of problems to which these results may be applied. Of particular importance is the fact that, within these limitations, it is not possible to consider any cases where there are appreciable interactions between the component systems of an assembly.

In order that the statistical method may be extended to a wider range of physical problems it is useful to introduce the concept of an *ensemble*. For this purpose consider a group of assemblies which all have the same volume and in which the component systems are all of the same type. Then, depending on the conditions imposed on the assemblies, there will be a large number of distinct arrangements of the systems (i.e. microstates*) within the assemblies. If, for each of these arrangements or microstates, there is at least one corresponding assembly in the group, then the group is said to form an ensemble. Now, since all the possible states of a particular assembly will be represented in the ensemble, the study of the ensemble will be equivalent to studying an assembly as the arrangement of its systems varies with time through all the possible microstates. The averaging of the assembly properties over the assemblies forming an ensemble will therefore give the same result as if this average were taken for a single assembly as its state varied with time.

* See footnote, p. 10.

In the present chapter consideration will be given to those assemblies which may be considered to form a *canonical ensemble.** In such an ensemble the number of systems is taken to be the same fixed quantity for each assembly but it is the temperature of the assemblies which is considered to be constant rather than the assembly energy. Under this condition it is possible to allow for the exchange of energy between assemblies in an ensemble and also to treat the interactions between the component systems within an assembly. It will be shown that the use of the canonical ensemble allows the treatment of fluctuations of certain of the properties of an assembly to be considered and an indication will be given of how this type of ensemble may lead to simultaneous statistical and quantum mechanical averages in those cases where the state of an assembly is described by a quantum mechanical wave-function.

The study of those assemblies in which both the energy and the number of systems may be allowed to vary will be left until the next chapter.

## 9.2. *The constant temperature ensemble*

Because the assemblies in a canonical ensemble are defined as being all at the same temperature, it is possible to consider that neighbouring assemblies within the ensemble are in thermal contact with each other. Then, when the assemblies are in a state of thermodynamic equilibrium, the complete ensemble may be considered as forming a constant temperature enclosure.

The form of this constant temperature ensemble may be illustrated as in Fig. 27 where the boundaries of the assemblies fix the

* In the case of the assemblies with fixed energy and a fixed number of systems which have been studied in the previous chapters, these assemblies are sometimes referred to as being members of a *microcanonical ensemble.* In such an ensemble all the assemblies are identical with respect to volume, energy and number and type of systems and they are isolated from each other and from their surroundings in all respects. There is no obvious advantage in using this concept in the present work although the Planck definition of entropy, mentioned in section 6.2, is sometimes given as

$$S = k \log \Omega$$

where $\Omega$ is the number of assemblies required to make up the ensemble, i.e. the total number of distinct arrangements of the systems within a given assembly.

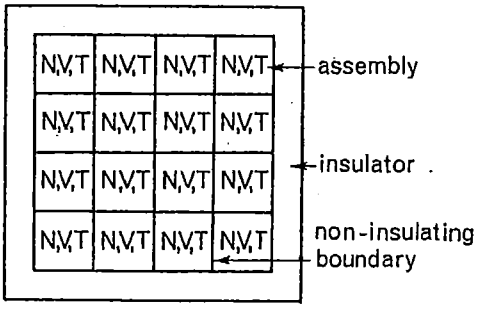


Fig. 27. The canonical or constant temperature ensemble.

number of systems, $N$, and the volume $V$ to be the same for each assembly. However, since these boundaries are permeable to the transfer of energy (or heat), they do not fix the energies of the assemblies and it is the temperature $T$ which is the same throughout the ensemble.* The energy of an assembly within the canonical ensemble may thus, theoretically, vary with time over all values from zero to the total energy of the ensemble.

Consider now that an assembly in a canonical ensemble is in a state $i$ such that its energy is $E_i$. This state $i$ will be defined by the values which the $6N$ coordinates of momentum and position of the $N$ systems take in this state. The probability that the assembly is in the state $i$, with the energy $E_i$, may be found by treating the individual assemblies in the ensemble as if they were themselves component 'systems' of a larger assembly. In this case the larger assembly will be the canonical ensemble which may be considered to have both fixed energy and temperature.† The assemblies of the canonical ensemble may now be taken to be of sufficient size so that the energy of any interactions between two of the assemblies is completely negligible compared with the total energy of the assemblies. Then, even though the interactions between the systems within an assembly may not be negligible, the assemblies themselves may be treated as non-interacting 'systems' in the larger assembly formed by the canonical ensemble.

* In the microcanonical ensemble the fixed quantities $N$, $V$ and $T$ would be replaced by $N$, $V$ and $E$ where $E$ is the assembly energy. It will therefore be clear that some of the applications given in Chapter 8 have, effectively, made use of the concept of the constant temperature ensemble.

† From this point of view the whole canonical ensemble is being considered as a single assembly and so could, in turn, be defined as a member of a microcanonical ensemble!

Taking the result obtained in equation 2.21 for the distribution of energies in a classical assembly, it is possible to write the probability that a component assembly will be in a state $i$ as

$$p_i = p(0)\, e^{-E_i/kT} \tag{9.1}$$

where $p(0)$ is a function of $T$, the temperature of the ensemble. (A result similar to that of equation 9.1 is obtained in Appendix 3 for the case of a completely classical ensemble, use being made of the Liouville theorem in the manner indicated by Gibbs. An alternative procedure involving the definition of entropy in terms of the available volume of phase space is given by Landau and Lifshitz in their book *Statistical Physics*.)

Because the assembly must be in one of the states represented by the suffix $i$ it is possible to write

$$\sum_i p_i = 1 \tag{9.2}$$

where the summation is taken over all the possible states $i$. Together with equation 9.1 this condition gives

$$p(0) \sum_i e^{-E_i/kT} = 1$$

from which it follows that the term $p(0)$ in equation 9.1 is given by

$$p(0) = \frac{1}{\sum_i e^{-E_i/kT}} \tag{9.3}$$

As with the assemblies previously considered it is again convenient to define a partition function for the assemblies in a canonical ensemble. By comparison with equation 7.5, this partition function is chosen as

$$\boxed{\mathbf{Z} = \sum_i e^{-E_i/kT}} \tag{9.4}$$

and is sometimes referred to as the *constant temperature partition function* of the ensemble. It will be seen, however, that this partition function has properties very similar to those of the *total* partition function defined by equation 7.31 although it must be remembered that the definition given there referred to the case of an assembly in which there were no interactions between the component systems. The term total partition function together

with the same symbol as in equation 7.31 will therefore be used for the partition function defined by equation 9.4.

Using equations 9.1, 9.3 and 9.4 the probability that an assembly is in the state $i$ becomes

$$p_i = \frac{e^{-E_i/kT}}{\mathbf{Z}} \qquad 9.5$$

## 9.3. *Thermodynamic properties of the canonical ensemble*

Consider that the energy states which are allowed to the assemblies in a canonical ensemble are the various values of $E_i$. Then, as given in equation 1.6*b*, the mean energy of an assembly in the ensemble is

$$\bar{E} = \sum_i p_i E_i \qquad 9.6$$

Using the value of $p_i$ from equation 9.5 this becomes, for an ensemble at temperature $T$,

$$\bar{E} = \frac{1}{\mathbf{Z}} \sum_i (e^{-E_i/kT} E_i) \qquad 9.7$$

Now $\sum_i (e^{-E_i/kT} E_i) = \dfrac{\partial}{\partial(-1/kT)} \left\{ \sum_i e^{-E_i/kT} \right\} \equiv kT^2 \dfrac{\partial \mathbf{Z}}{\partial T}$ so that equation 9.7 becomes

$$\bar{E} = \frac{kT^2}{\mathbf{Z}} \frac{\partial \mathbf{Z}}{\partial T} \qquad 9.8a$$

or

$$\bar{E} = kT^2 \frac{\partial \log \mathbf{Z}}{\partial T} \qquad 9.8b$$

(The quantity which is maintained constant in the partial differentiation of the equations 9.8 may be taken to be either the values of the energy levels $E_i$ or, which is generally equivalent, the volume of the assembly.)

The thermodynamic relationship between the free energy $F$ and the energy $E$ of an assembly was given in equation 6.18 in the form $E = -T^2 \left\{ \dfrac{\partial (F/T)}{\partial T} \right\}_V$. Substituting for this expression in

equation 9.8*b* gives

$$\frac{\partial(F/T)}{\partial T} = -k\frac{\partial \log \mathbf{Z}}{\partial T}$$

and the mean free energy is obtained as

$$F = -kT \log \mathbf{Z} + C \qquad 9.9$$

where $C$ is some function independent of the temperature. Now, if the relationships $F = E - TS$ and $S = -\{\partial F/\partial T\}_V$ are to give an unambiguous value for the entropy when the equations 9.8*b* and 9.9 are used, it is clearly necessary that $C$, the constant of integration, shall be zero. Therefore the free energy of an assembly becomes

$$\boxed{F = -kT \log \mathbf{Z}} \qquad 9.10$$

in agreement with equation 7.32. (Deriving $F$ from the value of $\bar{E}$ in equation 9.8*b* is justifiable since, in the consideration of the thermodynamic properties of the assembly, the mean free energy and the measured free energy will be the same quantity. The fluctuations about the mean value will be negligible for a normal assembly with a large number of systems (see section 9.5) and any large fluctuations will last for a period of time too short for a measurement to be made.)

Taking equation 9.10 in the form

$$\mathbf{Z} = e^{-F/kT} \qquad 9.11$$

the expression for the probability $p_i$ in equation 9.5 becomes

$$\boxed{p_i = e^{(F-E_i)/kT}} \qquad 9.12$$

This equation is sometimes taken as the definition of a canonical ensemble. That is, if the probability that an assembly is in a state $i$ with energy $E_i$ is given by an equation of the form 9.12, the assembly is said to be a member of a canonical ensemble.

As with any thermodynamic system, the entropy of an assembly in a canonical ensemble may be found by evaluating the differential $S = -\{\partial F/\partial T\}_V$. Using the value of the free energy given in equation 9.10 an expression in terms of the total partition function is obtained as

$$S = k\left\{\log \mathbf{Z} + \frac{T\partial \log \mathbf{Z}}{\partial T}\right\} \qquad 9.13$$

However, a different type of expression for the entropy may be obtained by using the alternative thermodynamic relation

$$S = \frac{E-F}{T}.$$

Writing the thermodynamic energy as $E = \sum_i p_i E_i$ and $F = F\sum_i p_i$ (since $\sum_i p_i = 1$) this latter expression gives

$$S = \sum_i p_i \frac{E_i - F}{T}$$

$$= -k\sum_i p_i \frac{F-E_i}{kT} \qquad 9.14$$

Now, from equation 9.12, it is possible to write $\{F-E_i\}/kT = \log p_i$ so that equation 9.14 gives

$$\boxed{S = -k\sum_i p_i \log p_i} \qquad 9.15$$

(This expression for the entropy is taken by some authors as the starting point for the treatment of all statistical mechanics problems.* The basis for so doing is that, since any formulae of statistical mechanics must be justified *a posteriori* in spite of the formal foundations which have been proposed, it is very useful to take as a starting point a postulate which is directly applicable to a wide range of assemblies and types of assemblies. The logical basis for taking equation 9.15 to be the fundamental equation of statistical physics lies in the study of information theory. In this theory it is possible to relate entropy and information, as is shown by Kinchin —see the bibliography.

The equivalence of the entropy as given by equation 9.15 and the Boltzmann definition of the entropy is illustrated in the problems at the end of the chapter.)

## 9.4. *The evaluation of the Total Partition Function*

In this section the summation and integration methods of determining the total partition function will be given for the classical

* See, for example, J. C. Slater: *Introduction to Chemical Physics*, McGraw-Hill Publishing Company, 1939.

and semi-classical cases only. It will be observed that the partition functions derived on the more general basis of the canonical ensemble are in agreement with those already obtained in Chapter 7.

## THE CLASSICAL PARTITION FUNCTION

Consider an assembly of $N$ distinguishable, non-interacting systems at temperature $T$. Let the energy sheets available to the systems in the assembly be enumerated as:

| | | | | | | |
|---|---|---|---|---|---|---|
| Energy of sheet: | $\epsilon_1$ | $\epsilon_2$ | $\epsilon_3$ | $\cdots$ | $\epsilon_s$ | $\cdots$ |
| Weight of sheet: | $g_1$ | $g_2$ | $g_3$ | $\cdots$ | $g_s$ | $\cdots$ |

Let the corresponding occupation numbers of the sheets for an assembly in the state $i$ be taken as:

| | | | | | | |
|---|---|---|---|---|---|---|
| Occupation number of sheet: | $n_1$ | $n_2$ | $n_3$ | $\cdots$ | $n_s$ | $\cdots$ |

where the allowed values of the occupation numbers are limited by the condition

$$\sum_s n_s = N \tag{9.16}$$

The total energy of the assembly when it is in the state $i$, as defined by the particular set of values of the occupation numbers, is

$$E_i = \sum_s n_s \epsilon_s \tag{9.17}$$

With the configuration corresponding to the state $i$ defined in this way, this state will have a weight $W_i$ equal to the number of distinct arrangements of the systems which are possible with the given set of occupation numbers. Since the systems are considered to be distinguishable the weight (or degeneracy) of the state $i$ is as given in equation 2.7 for a classical assembly, i.e.

$$W_i = N! \prod_s \left\{ \frac{g_s^{n_s}}{n_s!} \right\} \tag{9.18}$$

When this weight is included in the partition function defined by equation 9.4 the result is

$$\mathbf{Z} = \sum_i W_i e^{-E_i/kT} \tag{9.19}$$

where the sum is over all possible states $i$ of the assembly and the

term $e^{-E_i/kT}$ is now included $W_i$ times. Using equation 9.18 for the weight $W_i$ and putting $E_i = \sum_s n_s\epsilon_s$, equation 9.19 may be replaced by

$$Z = \sum_{(n_s)} N! \prod_s \left\{ \frac{g_s^{n_s}}{n_s!} \right\} \exp\left( - \sum_s n_s\epsilon_s/kT \right) \qquad 9.20$$

where the summation is now over all the possible sets of the occupation numbers, $n_1$, $n_2$, $n_3$, etc., which satisfy the condition of equation 9.16. Such a summation will necessarily include all the possible configurations and, hence, all the possible states of the assembly. The sum in equation 9.20 may now be evaluated exactly by noting the following expansions to the power $N$:

$$\text{(i)}\ (x_1+x_2)^N = \sum_n \frac{N!}{n!\,(N-n)!} x_1^n x_2^{N-n} = \sum_{(n_1+n_2)=N} \frac{N!}{n_1!\,n_2!} x_1^{n_1} x_2^{n_2}$$

where $n$, $n_1$ and $n_2$ take all values from 0 to $N$.

$$\text{(ii)}\ (x_1+x_2+x_3)^N = \sum_{(n_1+n_2+n_3)=N} \frac{N!}{n_1!\,n_2!\,n_3!} x_1^{n_1} x_2^{n_2} x_3^{n_3}$$

where the sum is over all the possible values of $n_1$, $n_2$ and $n_3$ which satisfy the condition $n_1+n_2+n_3 = N$. Finally,

$$\text{(iii)}\ \left| \sum_s x_s \right|^N = \sum_{(n_s)} \frac{N!}{\prod_s n_s!} \prod_s x_s^{n_s}$$

$$= \sum_{(n_s)} N! \prod_s \left\{ \frac{x_s^{n_s}}{n_s!} \right\} \qquad 9.21$$

where the summation is now over all the possible combinations of the integers $n_s$ which satisfy the condition $\sum n_s = N$.

Writing $x_s = g_s\, e^{-\epsilon_s/kT}$ in equation 9.21 gives, again under the condition $\sum_s n_s = N$,

$$\left( \sum_s g_s\, e^{-\epsilon_s/kT} \right)^N = \sum_{(n_s)} N! \prod_s \left\{ \frac{g_s^{n_s}\, e^{-n_s\epsilon_s/kT}}{n_s!} \right\}$$

$$= \sum_{(n_s)} N! \prod_s \left\{ \frac{g_s^{n_s}}{n_s!} \right\} \exp\left( - \sum_s n_s\epsilon_s/kT \right)$$

Comparison with equation 9.20 then shows that

$$\boxed{\mathbf{Z} = \left(\sum_s g_s e^{-\epsilon_s/kT}\right)^N} \qquad 9.22$$

In Chapter 7 the partition function for a *system* in an assembly was defined so that

$$\sum_s g_s e^{-\epsilon_s/kT} = Z \qquad (7.3)$$

and therefore equation 9.22 gives

$$\mathbf{Z} = Z^N$$

That this is of the form expected for the classical total partition function will be seen from a comparison of equations 9.11 and 7.12.

### THE SEMI-CLASSICAL PARTITION FUNCTION

When the systems in the assembly are indistinguishable, non-localized and non-interacting the weight given by equation 9.18 must be replaced by the semi-classical weight which was given in Chapter 7 as

$$W_i = \prod_s \left\{\frac{g_s^{n_s}}{n_s!}\right\} \qquad (7.24)$$

The total partition function in equation 9.19 then becomes

$$\mathbf{Z} = \sum_{(n_s)} \prod_s \left\{\frac{g_s^{n_s}}{n_s!}\right\} \exp\left(-\sum_s n_s\epsilon_s/kT\right)$$

$$= \frac{1}{N!} \sum_{(n_s)} N! \prod_s \left\{\frac{g_s^{n_s}}{n_s!}\right\} \exp\left(-\sum_s n_s\epsilon_s/kT\right)$$

Comparison of this expression with equations 9.20 and 9.22 gives

$$\mathbf{Z} = \frac{1}{N!}\left(\sum_s g_s e^{-\epsilon_s/kT}\right)^N \qquad 9.23$$

$$= \frac{Z^N}{N!}$$

in agreement with equation 7.31.

## PARTITION FUNCTION IN THE PRESENCE OF INTERACTIONS

The partition functions in the form given above cannot be evaluated unless there is negligible interaction between the systems in the assemblies. When the interactions between the systems are not negligible the energies of the systems will depend on their position coordinates as well as their momentum coordinates and, in this case, the partition function must be found by integrating over all possible values of the $6N$ coordinates of the systems.

Let $d\Gamma_{6N}$ be an element of volume in the $6N$-dimensional phase space of the $N$ systems of the assembly. The number of allowed states of the assembly which are described by the coordinates within this element of volume is given by equation A5.11 of Appendix 5 as $d\Gamma_{6N}/h^{3N}$. This quantity is equivalent to the weight $W$ for that assembly which has its systems in this state so that, if the energy of the assembly in this state is $E$ and the systems are considered to be distinguishable, then the partition function defined as $\sum_i W_i e^{-E_i/kT}$ becomes

$$\mathbf{Z} = \int_{\Gamma_{6N}} e^{-E/kT} \frac{d\Gamma_{6N}}{h^{3N}} \qquad 9.24$$

with the integral taken over all the available volume of phase space.

In the case where the systems are indistinguishable it is possible to arrange any given $N$ sets of three position and three momentum coordinates among the $N$ systems of the assembly in $N!$ ways without producing any additional distinguishable states of the assembly. Any state in a given volume element $d\Gamma_{6N}$ must therefore be counted only as $1/N!$ of a state in order to allow for this indistinguishability. The *semi-classical* partition function corresponding to equation 9.24 is thus

$$\mathbf{Z} = \int_{\Gamma_{6N}} e^{-E/kT} \frac{d\Gamma_{6N}}{h^{3N}N!} \qquad 9.25$$

which is in agreement with equation 7.44 when $d\Gamma_{6N}$ is set equal to $\prod_{j=1}^{N} dx_j dy_j dz_j dp_{xj} dp_{yj} dp_{zj}$. It is left as an exercise for the student to show that, in the absence of interactions, equation 9.25 reduces to the form $\mathbf{Z} = Z^N/N!$ where $Z = \dfrac{V(2\pi mkT)^{\frac{3}{2}}}{h^3}$.

## 9.5. *The energy distribution over the canonical ensemble*

The probability that an assembly at temperature $T$ is in an energy state $E_i$ has been shown above to be given by

$$p_i = e^{(F-E_i)/kT}$$

However, if it is required to calculate the probability that the assembly has an energy within the range $E$ to $E+dE$, account must be taken of the number of allowed states in this energy range as well as of the relevant value of $p_i$. Letting $\Omega'(E)\,dE$ be the number of allowed states of the assemblies which have energies within the range $E$ to $E+dE$, the number of assemblies having energies in this range will be

$$N(E)\,dE = e^{(F-E)/kT}\Omega'(E)\,dE$$

The form of $N(E)$ is shown, together with the other terms, in Fig. 28. The energy at the maximum of the curve of $N(E)$ will be very close to the mean energy of the assemblies since, as in section 2.4, the sharpness of this maximum is very pronounced.

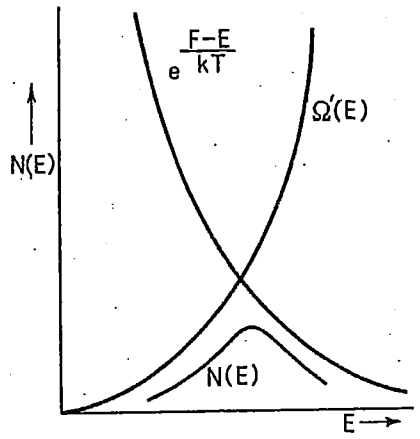


Fig. 28. Distribution of assemblies.

## 9.6. *Application of the canonical ensemble to an imperfect gas*

In order to illustrate one of the applications of the canonical ensemble consideration will now be given to the case of an imperfect gas in which the interactions between the, otherwise, semi-classical molecules are not negligible. The energy of such a gas will be made up of components which depend both on the momenta and on the positions of the molecules. If it is assumed that the energy of interaction between any two molecules is independent

of the momenta of the molecules and is also independent of the positions of the other molecules it is possible to write the total energy of the assembly as

$$E = \frac{1}{2m}\sum_{j=1}^{N}(p_{xj}^2+p_{yj}^2+p_{zj}^2)+\sum_{j=1}^{N}\sum_{l>j}U_{jl} \qquad 9.26$$

In this expression $N$ is the number of molecules, $p_{xj}$, etc., are the components of momentum of the $j$th molecule, $U_{jl}$ is the energy of interaction between the $j$th and $l$th molecules and the condition $l > j$ in the part of the double summation which is over all values of $l$ is to prevent the interaction energies being counted twice, once for $U_{jl}$ and once for $U_{lj}$. The partition function for the gas will be given by substituting the energy given by equation 9.26 into equation 9.25 so that

$$\mathbf{Z} = \frac{1}{N!\,h^{3N}}\int_{\Gamma_{6N}}\exp\left[-\sum_{j=1}^{N}\left\{\frac{1}{2m}(p_{xj}^2+p_{yj}^2+p_{zj}^2)+\sum_{l>j}U_{jl}\right\}\Big/kT\right]d\Gamma_{6N} \qquad 9.27$$

With $d\Gamma_{6N}$ written as $\prod_{j=1}^{N} dp_{xj}dp_{yj}dp_{zj}dx_jdy_jdz_j$, the integrations involving the components of the momentum may be evaluated independently, the limits being $-\infty$ to $+\infty$ for each component. Then, since each integral involving the momentum will have the same value,

$$\mathbf{Z} = \frac{1}{N!\,h^{3N}}\left\{\int_{-\infty}^{\infty}\exp(-p_{x_1}^2/2mkT)\,dp_{x_1}\right\}^{3N} \times\int_V\int_V\cdots\int_V\exp\left(-\sum_{j=1}^{N}\sum_{l>j}U_{jl}/kT\right)\times\prod_{j=1}^{N}dx_jdy_jdz_j$$

where the integrals involving the position coordinates are taken over the volume $V$ of the gas. Taking $\int_{-\infty}^{\infty}\exp(-\lambda x^2)\,dx = \sqrt{(\pi/\lambda)}$ from equation A6.11 of Appendix 6 the partition function becomes

$$\mathbf{Z} = \frac{(2\pi mkT)^{3N/2}}{N!\,h^{3N}}\int_V\int_V\cdots\int_V\exp\left(-\sum_{j=1}^{N}\sum_{l>j}U_{jl}/kT\right)\times\prod_{j=1}^{N}dx_jdy_jdz_j \qquad 9.28$$

With the $N$-fold integral over the position coordinates written as $I_N$ equation 9.28 becomes

$$\mathbf{Z} = \frac{(2\pi mkT)^{3N/2}}{N!\,h^{3N}} I_N \qquad 9.29$$

The equation of state of the gas is obtained by writing the free energy from equation 9.10 as

$$\begin{aligned} F &= -kT\log \mathbf{Z} \\ &= -kT\left[\log\left\{\frac{(2\pi mkT)^{3N/2}}{N!\,h^{3N}}\right\} + \log I_N\right] \end{aligned} \qquad 9.30$$

The pressure of the gas is then given by

$$p = -\left\{\frac{\partial F}{\partial V}\right\}_T$$

or

$$p = \frac{kT}{I_N}\left\{\frac{\partial I_N}{\partial V}\right\}_T \qquad 9.31$$

If the interactions between the molecules were negligible so that $e^{-U_{jl}/kT} \simeq 1$ for all $j$ and $l$, the integral $I_N$ in equation 9.28 would become

$$\begin{aligned} I_N &= \int_V \int_V \cdots \int_V \exp\left(-\sum_{j=1}^{N} \sum_{l>j} U_{jl}/kT\right) \\ &\quad \times \prod_{j=1}^{N} dx_j dy_j dz_j \\ &\simeq \prod_{j=1}^{N} \int_V dx_j dy_j dz_j \\ &= V^N \end{aligned} \qquad 9.32$$

Equation 9.31 then gives

$$\mathbf{p = \frac{NkT}{V}}$$

as expected for non-interacting, semi-classical molecules. (If account were taken of that volume $b$ of the gas which is not available to the molecules because of their finite volume then the integrals in equation 9.32 would be over the volume $(V-b)$ and the equation of state would become $p = NkT/(V-b)$. This result could, however, be obtained without reference to the canonical ensemble and is therefore not of particular interest here.)

The general form of the interaction energy $U_{jl}$ as a function of the separation $r_{jl}$ of the molecules $j$ and $l$ is shown in Fig. 29. If

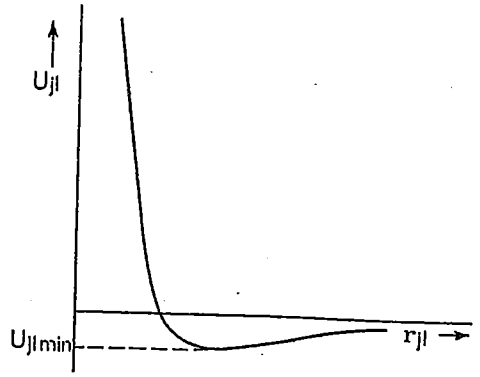


Fig. 29. Interaction energy as a function of molecule separation.

the magnitude of the minimum energy, $|U_{jl\,\min}|$, is very much less than the thermal energy $kT$ it is convenient to write for monatomic molecules,

$$e^{-U_{jl}/kT} = 1 + f(r_{jl})$$

where $f(r_{jl})$ is taken as a function of the temperature and of the separation of the molecules only. (For polyatomic molecules the energy $U_{jl}$, and hence $f(r_{jl})$, may be a function of the orientation of the molecules.) The exponential in the integral of equation 9.32 can be written in this approximation as

$$\exp\left(-\sum_{j=1}^{N}\sum_{l>j} U_{jl}/kT\right) = \prod_{l>j,\,j=1}^{j=N} \{1+f(r_{jl})\} \qquad 9.33$$

where the product involves all possible values of $l$ and $j$ except that the condition $l > j$ still applies. As a first approximation it will be considered that only the first two terms in this product are significant since it is being assumed that the interaction energies are small. Then

$$\prod_{l>j,\,j=1}^{j=N} \{1+f(r_{jl})\} \simeq 1 + \sum_{j=1}^{N}\sum_{l>j} f(r_{jl}) \qquad 9.34$$

Substituting from equations 9.33 and 9.34 into equation 9.32 gives

$$I_N = \int_V \int_V \cdots \int_V \left\{1 + \sum_{j=1}^{N}\sum_{l>j} f(r_{jl})\right\} \prod_{j=1}^{N} dx_j dy_j dz_j$$

$$= V^N + \int_V \int_V \cdots \int_V \sum_{j=1}^{N}\sum_{l>j} f(r_{jl}) \prod_{j=1}^{N} dx_j dy_j dz_j \qquad 9.35$$

Since it is assumed that the mutual energy of any two molecules is independent of the other $(N-2)$ molecules, the integral of $f(r_{jl})$ may be taken as being independent of all but the six coordinates $x_j, x_l ; y_j, y_l ; z_j, z_l$. Also, since the integrals are taken over the whole of the volume $V$, all the integrals will be the same independent of the particular molecules $j$ and $l$ considered. Then equation 9.35 gives

$$I_N = V^N + \frac{N(N-1)}{2} \int_V \int_V \cdots \int_V f(r_{jl}) \prod_{j=1}^{N} dx_j dy_j dz_j$$

$$= V^N + \frac{N(N-1)V^{N-2}}{2}$$

$$\times \int_V \int_V f(r_{jl})\, dx_j dy_j dz_j dx_l dy_l dz_l \qquad 9.36$$

since there are $\frac{1}{2}N(N-1)$ different combinations of the suffices $j$ and $l$. Let the origin of coordinates of the molecule $j$ be taken at the position of the molecule $l$ and assume that $f(r_{jl})$ falls to zero rapidly as $r_{jl}$ increases. Then, using spherical polar coordinates $r$, $\theta$ and $\phi$ (with $r = r_{jl}$) to give the position of the molecule $j$ relative to the molecule $l$ so that $dx_j dy_j dz_j$ may be replaced by $r^2\, dr \sin\theta\, d\theta d\phi$, the double integral in equation 9.36 may be written with the limit of $r$ taken as infinity so that

$$\int_V \int_V f(r_{jl})\, dx_j dy_j dz_j dx_l dy_l dz_l \simeq \int_V dx_l dy_l dz_l \int_0^{\pi} \sin\theta\, d\theta$$

$$\times \int_0^{2\pi} d\phi \int_0^{\infty} f(r) r^2\, dr$$

$$= V \int_0^{\infty} f(r) 4\pi r^2\, dr \qquad 9.37$$

The interaction integral obtained from equation 9.37 is independent of the position of the origin of coordinates and this is equivalent to the assumption that the volume $V$ is sufficiently large for the boundaries of the containing vessel to have a negligible effect on the properties of the gas.

Putting $\int_0^{\infty} f(r) 4\pi r^2\, dr = a$ and substituting in equation 9.36 gives

$$I_N = V^N + \frac{N(N-1)}{2} V^{N-1} a \qquad 9.38$$

The equation of state is obtained, on putting this value of $I_N$ in

equation 9.31, as

$$p = \frac{kT}{\left\{V^N + \frac{N(N-1)}{2} V^{N-1} a\right\} \times \left\{NV^{N-1} + \frac{N(N-1)^2}{2} V^{N-2} a\right\}}$$

or

$$p \simeq \frac{NkT}{V}\left(1 - \frac{(N-1)}{2}\frac{a}{V}\right) \qquad 9.39$$

If the energy of interaction $U_{ji}$ is small so that $e^{-U_{ji}/kT} \simeq 1 - U_{ji}/kT$ then $f(r_{ji}) \simeq -U_{ji}/kT$ and the constant $a$ introduced into equation 9.38 becomes $a = -(1/kT)\int_0^\infty U(r) 4\pi r^2 \, dr = a'/kT$ where $a'$ is positive since $U(r)$ will be negative in the region of interest. Then equation 9.39 can be rewritten with $a/V = a'/kTV \simeq a'N/pV^2$ to give

$$p \simeq \frac{NkT}{V}\left(1 - \frac{(N-1)}{2}\frac{Na'}{pV^2}\right)$$

or

$$\left(p + \frac{a''}{V^2}\right) V \simeq NkT$$

where $a'' = (N-1)Na'/2$. If we correct, to first order, for the effective volume $b$ of the molecules so that $V$ is replaced by $(V-b)$, we see that the equation is equivalent to that given by Van der Waals.

Because of the assumptions which have been made this equation of state will only be applicable in the case of very small energies of interaction between the molecules. If a more meaningful expression is to be obtained it is necessary to take into account higher order terms of the product in equation 9.34 and to allow for the effect of 'clusters' of molecules.* However, the process by which equation 9.39 was obtained is used here solely to indicate one form of application of the canonical ensemble.

## 9.7. *Fluctuations of the assembly energy in a canonical ensemble*

When an assembly is in a constant temperature enclosure the energy of the assembly can fluctuate about its mean value as heat

* See for example, G. S. Rushbrooke: *Introduction to Statistical Mechanics*, O.U.P.

is absorbed from or given to its surroundings. The calculation of the magnitude of the energy fluctuations in such an assembly may be performed using the concept of the canonical ensemble.

Let the deviation of the energy of an assembly from its mean value, $\bar{E}$, be defined as

$$\delta E = E - \bar{E} \tag{9.40}$$

From the definition of the mean energy it follows that the mean value of this deviation $\delta E$ will be zero. A meaningful measurement of the magnitude of the energy fluctuations may be taken as the mean square deviation defined as $\overline{(\delta E)^2}$. Using equation 9.40 this mean square deviation is given by

$$\begin{aligned}\overline{(\delta E)^2} &= \overline{(E-\bar{E})^2} \\ &= \overline{(E^2 - 2E\,.\,\bar{E} + \bar{E}^2)} \\ &= \overline{E^2} - 2\bar{E}\,.\,\bar{E} + \bar{E}^2\end{aligned}$$

or

$$\overline{(\delta E)^2} = \overline{E^2} - \bar{E}^2 \tag{9.41}$$

Now, with the definition of the mean energy $\bar{E} = \sum_i p_i E_i$ as given in equation 9.6, the result obtained in equation 9.8*a* was

$$\bar{E} = \frac{kT^2}{\mathbf{Z}} \frac{\partial \mathbf{Z}}{\partial T}$$

or

$$\bar{E} = \frac{1}{\mathbf{Z}} \frac{\partial \mathbf{Z}}{\partial \beta} \tag{9.42}$$

with $\beta = -1/kT$. Similarly the mean square energy may be written as

$$\overline{E^2} = \sum_i p_i E_i^2$$

Then, with $p_i = e^{-E_i/kT}/\mathbf{Z}$ from equation 9.5,

$$\begin{aligned}\overline{E^2} &= \frac{1}{\mathbf{Z}} \sum_i (e^{-E_i/kT} E_i^2) \\ &= \frac{1}{\mathbf{Z}} \frac{\partial^2}{\partial(-1/kT)^2} \sum_i e^{-E_i/kT}\end{aligned}$$

which gives

$$\overline{E^2} = \frac{1}{\mathbf{Z}} \frac{\partial^2 \mathbf{Z}}{\partial \beta^2} \tag{9.43}$$

If the expression for the mean energy given in equation 9.42 is differentiated with respect to $\beta$ the result is

$$\frac{\partial \bar{E}}{\partial \beta} = \frac{1}{\mathbf{Z}} \frac{\partial^2 \mathbf{Z}}{\partial \beta^2} - \frac{1}{\mathbf{Z}^2} \left\{ \frac{\partial \mathbf{Z}}{\partial \beta} \right\}^2 \tag{9.44}$$

On substituting from equations 9.42 and 9.43, this equation 9.44 becomes

$$\frac{\partial \bar{E}}{\partial \beta} = \overline{E^2} - \bar{E}^2 \tag{9.45}$$

Comparison of equation 9.45 with equation 9.41 shows that

$$\overline{(\delta E)^2} = \frac{\partial \bar{E}}{\partial \beta} \tag{9.46}$$

Rewriting the differential in this expression as $\partial \bar{E}/\partial \beta = kT^2(\partial \bar{E}/\partial T)$ and putting $\partial \bar{E}/\partial T = C_v$, the specific heat at constant volume, equation 9.46 becomes

$$\overline{(\delta E)^2} = kT^2 C_v \tag{9.47}$$

A useful definition of the mean fractional energy fluctuation may be taken as

$$\mathscr{F} = \left\{ \frac{\overline{(\delta E)^2}}{\bar{E}^2} \right\}^{\frac{1}{2}} = \left\{ \frac{kT^2 C_v}{\bar{E}^2} \right\}^{\frac{1}{2}} \tag{9.48}$$

For a perfect monatomic gas $C_v = \frac{3}{2}Nk$ and $\bar{E} = \frac{3}{2}NkT$ so that equation 9.48 gives for this case

$$\mathscr{F} = \left\{ \frac{\frac{3}{2}Nk^2T^2}{(\frac{3}{2}NkT)^2} \right\}^{\frac{1}{2}}$$

$$= (\tfrac{3}{2}N)^{-\frac{1}{2}} \tag{9.49}$$

If the sample of gas under consideration is at S.T.P. and has a volume of 1 cm$^3$ there will be about $3 \times 10^{19}$ molecules in the gas and the mean fractional energy fluctuation given by equation 9.49 will be

$$\mathscr{F} \simeq 2 \times 10^{-10}$$

which is negligible for most purposes. Clearly, since $\mathscr{F} \propto N^{-\frac{1}{2}}$, the smaller the sample of the gas which is under consideration the

larger, and more important, will be the fractional fluctuation in the energy of the sample.

## 9.8. *The quantum mechanical density operator*

At this point it is of interest to consider the application of the canonical ensemble to a quantum mechanical assembly which may be described by a time-independent wave-function $\psi$. This application will, to some extent, illustrate the statistical nature of the quantum mechanical method and will involve the expression of the probability function $p_i$ of equations 9.1 and 9.12 in terms of a quantum mechanical operator.

Suppose that the wave-function $\psi$ describes an assembly of $N$ systems and is a function of the $3N$ position coordinates of these systems. The wave-function will be a solution of the differential equation

$$\mathscr{H}\psi = E\psi \qquad 9.50$$

where $E$ is the energy and $\mathscr{H}$ is the Hamiltonian operator of the assembly. (For the present purpose this Hamiltonian operator may be taken as

$$\mathscr{H} = -\frac{h^2}{8\pi^2 m}(\nabla_1^2+\nabla_2^2+\ldots+\nabla_j^2+\ldots+\nabla_N^2)$$

$$+U(x_1, y_1, z_1, \ldots, x_N, y_N, z_N)$$

where $\nabla_j^2$ is the differential operator $\left\{\frac{\partial^2}{\partial x_j^2}+\frac{\partial^2}{\partial y_j^2}+\frac{\partial^2}{\partial z_j^2}\right\}$ for the $j$th system, $U$ is the potential energy of the assembly as a function of the spatial coordinates and $m$ is the mass per system.) Equation 9.50 then defines both the allowed energies of the assembly (the energy eigenvalues) and the corresponding allowed wave-functions (the eigenfunctions).

If one of these eigenfunctions is $\psi_i$ and its corresponding energy eigenvalue is $E_i$ then these must, of course, satisfy the equation

$$\mathscr{H}\psi_i = E_i\psi_i \qquad 9.51$$

It is now useful to define a wave-mechanical differential operator, $\not{p}$, corresponding to the probability function $p_i$, where $p_i$ now gives the probability that the assembly will be in the state

with wave-function $\psi_i$ and the energy eigenvalue $E_i$. This, so called, density operator* may be defined such that, for all $\psi_i$,

$$\not{\rho}\psi_i = p_i\psi_i \qquad 9.52$$

Because $p_i$ has been shown to be a function of the energy $E_i$ it is reasonable to assume that $\not{\rho}$ may be expressed as a function of the Hamiltonian operator $\mathcal{H}$.

Suppose that the density operator can be written as a polynomial in $\mathcal{H}$, i.e.

$$\not{\rho} = a_0 + a_1\mathcal{H} + a_2\mathcal{H}^2 + a_3\mathcal{H}^3 + \ldots \qquad 9.53$$

where $a_0$, $a_1$, etc., are constants. Now it is possible to write

$$\mathcal{H}^n\psi = \mathcal{H}^{n-1}(\mathcal{H}\psi)$$

which becomes, on writing $\mathcal{H}\psi = E\psi$ from equation 9.50 for allowed wave-functions,

$$\mathcal{H}^n\psi = E\mathcal{H}^{n-1}\psi$$

By successive application of this procedure the result is obtained that

$$\mathcal{H}^n\psi = E^n\psi \qquad 9.54$$

Therefore, if the operator $\not{\rho}$ of equation 9.53 is applied in equation 9.52, it follows that

$$\begin{aligned}\not{\rho}\psi_i &= (a_0 + a_1\mathcal{H} + a_2\mathcal{H}^2 + a_3\mathcal{H}^3 + \ldots)\psi_i \\ &= (a_0 + a_1E_i + a_2E_i^2 + a_3E_i^3 + \ldots)\psi_i \qquad 9.55\end{aligned}$$

However, from the definition in equation 9.52,

$$\not{\rho}\psi_i = p_i\psi_i$$

where $p_i$ is known to be a function of $E_i$. It is therefore clear that the operator $\not{\rho}$ is the same function of $\mathcal{H}$ as $p_i$ is of $E_i$ and, taking $p_i$ from equation 9.12 as $e^{(F-E_i)/kT}$, the density operator will be given by

$$\not{\rho} = e^{(F-\mathcal{H})/kT} \qquad 9.56$$

(The exponential involving the operator $\mathcal{H}$ here implies simply the normal polynomial expansion of the form $e^x = 1 + x + x^2/2! + \ldots.$)

* The term density here refers to the fact that this operator will give the probability density of finding states defined by the functions $\psi_i$.

The usefulness of the density operator can be seen from the consideration of the average value of some property $Q$ of an assembly. Suppose that this property can be expressed as a function of the momentum and position coordinates of the systems and further suppose that an operator $\mathcal{Q}$ can be obtained from $Q$ by the **normal substitution** of $\frac{h}{2\pi i}\frac{\partial}{\partial x_1}$ for $p_{x1}$, $\frac{h}{2\pi i}\frac{\partial}{\partial y_1}$ for $p_{y1}$ and so on. Then, with the assembly in the state represented by the eigenfunction $\psi_i$, the expectation value of $Q$ for this state of the assembly is given by the quantum mechanical average

$$\langle Q\rangle_i = \int_\tau \psi_i^* \mathcal{Q} \psi_i \, d\tau \qquad 9.57$$

where $\psi_i^*$ is the complex conjugate of $\psi_i$ and the integral is taken over all possible values of the position coordinates so that $d\tau = \prod_{j=1}^{N} dx_j dy_j dz_j$ and $\tau = \int d\tau$. (It is assumed here that the wave-functions, $\psi$, are members of a set of normalized, orthogonal functions.)

The average value of $Q$ over the ensemble is, by definition,

$$\bar{Q} = \langle \bar{Q}\rangle_i = \sum_i p_i \langle Q\rangle_i$$

Using equation 9.57 this average becomes

$$\bar{Q} = \sum_i p_i \int_\tau \psi_i^* \mathcal{Q} \psi_i \, d\tau$$

$$= \sum_i \int_\tau \psi_i^* \mathcal{Q} p_i \psi_i \, d\tau$$

and

$$\boxed{\bar{Q} = \sum_i \int_\tau \psi_i^* \mathcal{Q} \not{p} \psi_i \, d\tau} \qquad 9.58$$

where use has been made of the identity $p_i\psi_i = \not{p}\psi_i$ given in equation 9.52.

**The averaging process represented in equation 9.58 includes the statistical nature** of the thermodynamic ensemble through the summation over the states $i$ while the statistical nature of the quantum mechanical wave-function is included through the integration over all values of the coordinates.

(If the wave-functions $\psi$ are not members of an orthonormal set—i.e. do not satisfy the conditions $\int_\tau \psi_i^* \psi_i \, d\tau = 1$ and $\int_\tau \psi_i^* \psi_j \, d\tau = 0$—it is possible to obtain from the density operator a set of probability functions $p_{ij}$ which form a density matrix. The discussion of the application of the density matrix to statistical mechanics must, however, be left to a more advanced treatise—see, for example, R. C. Tolman: *Principles of Statistical Mechanics.*)

## PROBLEMS

1. Show that the definition of the entropy as $S = -k \sum_i p_i \log p_i$ leads to the normal canonical distribution, $p_i = e^{(F - E_i)/kT}$ when the condition $\bar{E} = \sum_i p_i E_i$ is imposed and the entropy is written as $(\bar{E} - F)/T$.

2. Assuming that there are $W$ equally probable states of an assembly so that $p_i = 1/W$ for all values of $i$, show that the entropy as defined by equation 9.15 becomes $S = k \log W$.

3. Using Stirling's approximation find the value of the largest term in the summation of equation 9.20. Show that there would be very little error in assuming that the partition function of equation 9.20 is given using this largest term rather than the complete summation.

4. Use equation 9.58 with the Hamiltonian operator $\mathcal{H}$ in place of the operator $\mathcal{Q}$ to obtain the expression $\sum_i p_i E_i$ for the mean energy of an assembly.

Chapter 10

# The Grand Canonical Ensemble

In the previous chapter consideration was given to the properties of the canonical ensemble, the component assemblies of which are allowed to exchange energy amongst themselves. However, from its definition, the canonical ensemble must consist of closed assemblies, i.e. of assemblies containing a fixed number of systems.

Therefore, if it is required to treat an open assembly in which the number of systems is not a fixed quantity, it is necessary to work with a different type of ensemble—termed the *grand canonical ensemble.* This latter type of ensemble, consisting of open assemblies, is of particular importance in the consideration of, for example, chemical reactions.

The form of the grand canonical ensemble is illustrated schematically in Fig. 30 where only the temperature $T$ and the volume $V$ of the assemblies are considered to be fixed while there may be an interchange of both energy and systems between neighbouring assemblies.

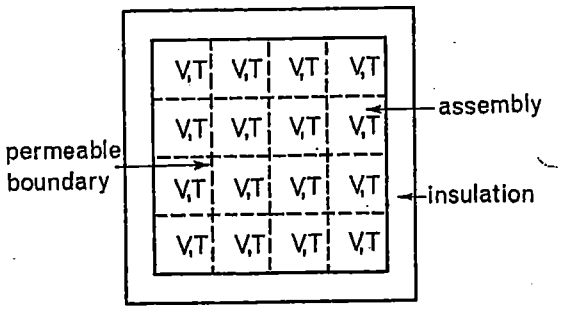


Fig. 30. The grand canonical ensemble.

Because, in this case, the number of systems in an assembly is not considered to be a fixed quantity, it is necessary to consider the effect of possible changes in these numbers on the thermodynamic functions of the open assemblies. It will be seen that the principal results obtained previously for the closed assemblies are now obtained in a more general manner.

## 10.1. *Thermodynamic functions of an open assembly*

In the case of a closed assembly the first law of thermodynamics has the form

$$dE = dQ - d\mathbf{W}$$

where $dQ$ is the heat added to the assembly, $d\mathbf{W}$ is the work done by the assembly and $dE$ is the resulting increase in the total energy of the assembly. For a reversible change of the state of the assembly in which the only work done is that due to a change in the volume of the assembly from $V$ to $V+dV$ this equation may be written in the familiar form

$$dE = T\,dS - p\,dV \qquad 10.1$$

where $p$ is the pressure acting on the assembly and the exact differentials $dS$ and $dV$ replace the inexact differentials $dQ$ and $d\mathbf{W}$.

When the number of systems in the assembly is no longer a fixed quantity an allowance must be made for the energy which will be contributed when a system is added to the assembly. If the addition of a single system to an open assembly increases the energy of the assembly by an amount $\mu$ then, for this case, equation 10.1 must be replaced by

$$dE = T\,dS - p\,dV + \mu\,dN \qquad 10.2$$

where $dN$ is the change in the number of component systems accompanying the change of state. (If there is more than one type of system in the assembly it will be necessary to write equation 10.2 as

$$dE = T\,dS - p\,dV + \sum_t \mu_t\,dN_t \qquad 10.3$$

where the summation is over the suffix $t$ which indicates the different types of systems. One of the elementary implications of equation 10.3 will be considered in section 10.5.)

Consider now that the assembly of entropy $S$, volume $V$ and number of systems $N$ is built up from nothing while the intensive variables—i.e. temperature $T$, pressure $p$, and $\mu$—are maintained constant. From equation 10.2 the total energy will then be

$$E = TS - pV + \mu N \qquad 10.4$$

The free energy of the assembly given by $F = E - TS$ is therefore

$$F = \mu N - pV \qquad 10.5$$

Now the Gibb's thermodynamic potential (or Gibb's free energy) is defined in thermodynamics as

$$G = E - TS + pV$$
$$= F + pV$$

so that, with equation 10.5, this thermodynamic function may be written

$$G = \mu N \tag{10.6}$$

The parameter $\mu$ may thus be considered as the Gibb's thermodynamic potential per system or, as it is called, the *chemical potential* of the systems.

Again considering the differential forms of the thermodynamic equations it is possible to write equation 10.2 as

$$T\,dS = dE + p\,dV - \mu\,dN \tag{10.7}$$

or

$$dS = \frac{1}{T}dE + \frac{p}{T}dV - \frac{\mu}{T}dN \tag{10.8}$$

Then, since $dE$, $dV$ and $dN$ are all exact differentials, their coefficients may be written in terms of the partial differentials so that:

$$\left\{\frac{\partial S}{\partial E}\right\}_{V,N} = \frac{1}{T} \tag{10.9a}$$

$$\left\{\frac{\partial S}{\partial V}\right\}_{E,N} = \frac{p}{T} \tag{10.9b}$$

and

$$\left\{\frac{\partial S}{\partial N}\right\}_{E,V} = -\frac{\mu}{T} \tag{10.9c}$$

Referring back to equation 2.13 it will be remembered that the condition for the most probable configuration of an assembly was given as

$$d \log W + \alpha\,dN + \beta\,dE = 0 \tag{2.13}$$

where $\alpha$ and $\beta$ were Lagrange undetermined multipliers and the volume of the assembly is assumed to remain constant. Applying the Boltzmann definition of the entropy as $S = k \log W$ this condition may be seen to be equivalent to writing

$$dS + \alpha k\,dN + \beta k\,dE \equiv 0 \tag{10.10}$$

so that, in this case,

$$\left\{\frac{\partial S}{\partial N}\right\}_{E,V} = -\alpha k \qquad 10.11$$

Comparison of equation 10.11 with equation 10.9*c* shows that the multiplier $\alpha$ and the chemical potential are related by the expression

$$\boxed{\alpha = \frac{\mu}{kT}} \qquad 10.12$$

## 10.2. *The Grand Partition Function*

In the grand canonical ensemble the state $i$ of an assembly will be defined in terms of both the energy $E_i$ and the number of systems, $N_i$, which the assembly has in this state. Clearly, then, the probability $p_i$ that the assembly is found to be in the state $i$ will be a function of both $E_i$ and $N_i$. The result obtained for $p_i$ in equation A3.20 of Appendix 3 is in agreement with this conclusion, i.e.

$$p_i = e^{(\chi + \xi N_i - E_i)/\theta} \qquad \text{(A3.20)}$$

where $\chi$, $\xi$ and $\theta$ are undefined thermodynamic functions. Comparison of this expression with the form of $p_i$ given in equation 9.12 for the canonical ensemble, namely

$$p_i = e^{(F - E_i)/kT} \qquad (9.12)$$

suggests that it would be reasonable to set $\chi + \xi N_i = F$ and $\theta = kT$. However, from equation 10.5, it is seen that $F = \mu N - pV$ so that it would be possible, in this case, to identify $\chi$ with $(-pV)$ and $\xi$ with the chemical potential $\mu$. The probability that the assembly is found in the state $i$ then becomes*

$$\boxed{p_i = e^{[-pV + (\mu N - E)_i]/kT}} \qquad 10.13$$

where $(\mu N - E)_i \equiv \mu N_i - E_i$. In this context the quantity $\chi = -pV$ is referred to as the *grand potential* of the assembly.

* The justification of this expression will again lie in the results which it predicts.

If the normalization condition

$$\sum_i p_i = 1$$

is applied to equation 10.13 it follows that

$$e^{-pV/kT} \sum_i e^{(\mu N - E)_i/kT} = 1 \qquad 10.14$$

Then

$$e^{-pV/kT} = \frac{1}{\sum_i e^{(\mu N - E)_i/kT}}$$

$$= \frac{1}{\mathcal{Z}} \qquad 10.15$$

where the *grand partition function* $\mathcal{Z}$ is defined as

$$\mathcal{Z} = \sum_i e^{(\mu N - E)_i/kT} \qquad 10.16$$

With this definition of the partition function it is possible to write equation 10.13 as

$$p_i = \frac{e^{(\mu N - E)_i/kT}}{\mathcal{Z}} \qquad 10.17$$

(It is sometimes convenient to use an alternative expression for the partition function in equation 10.16. This is obtained by writing

$$\mathcal{Z} = \sum_{N=0}^{\infty} \sum_i e^{(\mu N - E_{i,N})/kT} \qquad 10.18$$

where the summation is carried out for all the possible states $i$ of an assembly of $N$ systems and then for all values of $N$ from zero to infinity. The energy $E_{i,N}$ is then simply the energy of the state $i$ of an assembly of $N$ systems.)

If the quantity $-k\sum_i p_i \log p_i$ is evaluated as in equation 9.15, with $p_i$ taken from equation 10.13, then

$$-k\sum_i p_i \log p_i = -k\sum_i p_i \left\{\frac{-pV + (\mu N - E)_i}{kT}\right\}$$

$$= \frac{pV - \mu\bar{N} + \bar{E}}{T} \qquad 10.19$$

where $\bar{N}$ is the mean number of systems and $\bar{E}$ is the mean energy of an assembly. Now, from equation 10.4, it is possible to obtain the thermodynamic identity

$$TS = pV - \mu N + E$$

so that, with the thermodynamic averages equated to $\bar{N}$ and $\bar{E}$, equation 10.19 becomes

$$\boxed{S = -k \sum_i p_i \log p_i}$$

as for the canonical ensemble.

Finally, in this section, let it be considered how the thermodynamic properties of an assembly may be derived in terms of the grand potential. It will be seen from equation 10.4 that the product $(pV)$ may be written, with the thermodynamic average $\bar{N}$ replacing $N$, as

$$(pV) = TS + \mu\bar{N} - E$$

which becomes, on differentiating,

$$d(pV) = TdS + S\,dT + \mu\,d\bar{N} + \bar{N}\,d\mu - dE$$

Now equation 10.2 can be taken as $dE = TdS - p\,dV + \mu\,d\bar{N}$ so that

$$d(pV) = p\,dV + S\,dT + \bar{N}\,d\mu \qquad 10.20$$

The partial differentials obtained from equation 10.20 are

$$p = \left\{\frac{\partial(pV)}{\partial V}\right\}_{T,\mu} \qquad 10.21a$$

$$S = \left\{\frac{\partial(pV)}{\partial T}\right\}_{V,\mu} \qquad 10.21b$$

$$\bar{N} = \left\{\frac{\partial(pV)}{\partial \mu}\right\}_{T,V} \qquad 10.21c$$

(The number $\bar{N}$ here is, of course, the thermodynamic average of the number of systems in a given assembly in the ensemble.)

With these expressions it is now possible for the variables $p$, $S$ and $\bar{N}$ to be written in terms of the grand partition function $\mathcal{Z}$. From equation 10.15 the product $(pV)$ may be written as

$$(pV) = kT \log \mathcal{Z} \qquad 10.22$$

so that, for example, equation 10.21*c* becomes

$$\bar{N} = kT\left\{\frac{\partial \log \mathcal{Z}}{\partial \mu}\right\}_{T,V} \qquad 10.23$$

(An alternative, more direct method of obtaining the same result is to use the definition of $\bar{N}$ as

$$\bar{N} = \sum_i p_i N_i \qquad 10.24$$

Taking $p_i$ from equation 10.17 this becomes

$$\bar{N} = \frac{\sum_i e^{(\mu N_i - E_i)/kT} N_i}{\mathcal{Z}}$$

$$\equiv \frac{kT}{\mathcal{Z}}\left\{\frac{\partial}{\partial \mu}\sum_i e^{(\mu N_i - E_i)/kT}\right\}_{T,V}$$

$$= \frac{kT}{\mathcal{Z}}\left\{\frac{\partial \mathcal{Z}}{\partial \mu}\right\}_{T,V}$$

which is identical with equation 10.23.)

## 10.3. *Evaluation of the Grand Partition Function*

The grand partition function will now be evaluated for three cases; a semi-classical gas, a Bose–Einstein assembly and a Fermi–Dirac assembly. (It is not possible to give a proper treatment of the open classical assembly in which the systems are to be strictly distinguishable.)

### THE SEMI-CLASSICAL GRAND PARTITION FUNCTION BY SUMMATION OVER STATES

Consider an assembly in which the systems are distributed over the possible energy sheets so that there are $n_s$ systems in the sheet $s$ with energy $\epsilon_s$. If this configuration corresponds to the state $i$ then the energy of this state will be

$$E_i = \sum_s n_s \epsilon_s \qquad 10.25$$

and the number of systems in the assembly in this state will be

$$N_i = \sum_s n_s \qquad 10.26$$

Using these values of $E_i$ and $N_i$ the grand partition function defined

in equation 10.16 becomes

$$\mathcal{Z} = \sum_i W_i \exp[(\mu \sum_s n_s - \sum_s n_s \epsilon_s)/kT] \qquad 10.27$$

where $W_i$ is the weight of the state, or configuration, defined by the given set of occupation numbers $n_s$ and the summation over the states $i$ includes all possible sets of values of $n_s$. In the semi-classical case the weight of the configuration is given by equation 7.24 as

$$W_i = \left\{ \prod_s \frac{g_s^{n_s}}{n_s!} \right\}_i$$

where $g_s$ is the weight of the sheet $s$ and the suffix $i$ indicates the particular set of $n_s$ values. Equation 10.27 may thus be written as

$$\mathcal{Z} = \sum_{(n_s)} \left\{ \prod_s \frac{g_s^{n_s}}{n_s!} \right\} \exp[\sum_s n_s(\mu - \epsilon_s)/kT] \qquad 10.28$$

$$= \sum_{(n_s)} \prod_s \frac{(g_s e^{(\mu - \epsilon_s)/kT})^{n_s}}{n_s!} \qquad 10.29$$

where the summation is shown as being again over all possible sets of the occupation numbers $n_s$.

Now, it was shown in equation 9.21 that, for a set of quantities $x_1, x_2, x_3, \ldots, x_s, \ldots,$

$$(\sum_s x_s)^N = \sum_{\sum_s n_s = N} N! \prod_s \frac{x_s^{n_s}}{n_s!}$$

where the sets of the values of the numbers $n_s$ are only limited by the condition $\sum_s n_s = N$ and the summation is over all such sets. This equation may be rewritten so that

$$\sum_{\sum_s n_s = N} \prod_s \frac{x_s^{n_s}}{n_s!} = \frac{(\sum_s x_s)^N}{N!} \qquad 10.30a$$

However, if, as in equation 10.29, it is required that there shall be no limitation on the numbers $n_s$ in equation 10.30*a*, then allowance must be made for $\sum_s n_s$ to take all values from zero to infinity. Equation 10.30*a* then gives

$$\sum_{(n_s)} \prod_s \frac{x_s^{n_s}}{n_s!} = \sum_{N=0}^{\infty} \frac{(\sum_s x_s)^N}{N!} \qquad 10.30b$$

where $\sum_{(n_s)}$ indicates a summation over *all* sets of values of the numbers $n_s$. Substituting from equation 10.30*b* into equation 10.29, with $x_s = g_s\, e^{(\mu-\epsilon_s)/kT}$, gives

$$\mathcal{Z} = \sum_{N=0}^{\infty} \frac{[\sum_s g_s\, e^{(\mu-\epsilon_s)/kT}]^N}{N!} \qquad 10.31$$

By the definition of the partition function per system given in equation 7.4 it is possible to write $\sum_s g_s\, e^{-\epsilon_s/kT} = Z$, that is

$$\sum_s g_s e^{(\mu-\epsilon_s)/kT} = Z e^{\mu/kT} \qquad 10.32$$

Substituting from equation 10.32 into equation 10.31 gives, for the semi-classical case,

$$\mathcal{Z} = \sum_{N=0}^{\infty} \frac{(Ze^{\mu/kT})^N}{N!}$$

or, which is equivalent,

$$\boxed{\mathcal{Z} = \exp(Ze^{\mu/kT})} \qquad 10.33$$

The mean number of systems in the assembly is then given by equation 10.23 as

$$\bar{N} = kT\left\{\frac{\partial \log \mathcal{Z}}{\partial \mu}\right\}_{V,T}$$

$$= kT\left\{\frac{\partial (Ze^{\mu/kT})}{\partial \mu}\right\}_{V,T}$$

so that

$$\bar{N} = Ze^{\mu/kT} \qquad 10.34$$

Writing $Z = \sum_s g_s e^{-\epsilon_s/kT}$ and $\bar{N} = \sum_s \bar{n}_s$, where $\bar{n}_s$ is the number of systems in the sheet $s$ in the equilibrium (or mean) state of the assembly, equation 10.34 becomes

$$\sum_s \bar{n}_s = \sum_s g_s e^{(\mu-\epsilon_s)/kT} \qquad 10.35$$

For this equality to hold over all such summations there must be

an equivalence between the corresponding terms in the equation. It follows, therefore, that

$$\overline{n_s} = g_s e^{(\mu - \epsilon_s)/kT} \qquad 10.36$$

or, with $\mu/kT = \alpha$ as given in equation 10.12,

$$\overline{n_s} = g_s e^{\alpha - \epsilon_s/kT} \qquad 10.37$$

in agreement with the previously derived Maxwell–Boltzmann distribution.

### THE SEMI-CLASSICAL GRAND PARTITION BY INTEGRATION OVER PHASE SPACE

Now consider that the interactions between the systems in an assembly cannot be neglected. In this case it will not be possible to express the energy of the assembly as the sum of the independent energies of the systems and it is necessary to express the partition function as an integral over phase space rather than as a summation.

Let there be $N$ systems in the assembly under consideration and let the $6N$ position and momentum coordinates be in the element of phase space $d\Gamma_{6N}$. The energy of the assembly in this state can be taken as $E(N)$ and the number of states corresponding to the volume $d\Gamma_{6N}$ can be taken, as in equation 9.25, as $d\Gamma_{6N}/N!\,h^{3N}$. The partition function defined in equation 10.18 can thus be written in the integral form

$$\mathcal{Z} = \sum_{N=0}^{\infty} \int_{\Gamma_{6N}} e^{[\mu N - E(N)]/kT} \frac{d\Gamma_{6N}}{N!\,h^{3N}} \qquad 10.38$$

where $E(N)$ is expressed as a function of the $3N$ momentum coordinates and $3N$ position coordinates. Taking the factors which are independent of the $6N$ coordinates outside the integral sign, equation 10.38 becomes

$$\boxed{\mathcal{Z} = \sum_{N=0}^{\infty} \frac{e^{\mu N/kT}}{N!\,h^{3N}} \int_{\Gamma_{6N}} e^{-E(N)/kT}\, d\Gamma_{6N}} \qquad 10.39$$

This general equation for the semi-classical grand partition function will, of course, reduce to equation 10.33 when the energy of the interactions between the systems can be neglected.

## THE BOSE–EINSTEIN GRAND PARTITION FUNCTION

Consider first the product

$$\prod_j (1-x_j)^{-1} = (1-x_1)^{-1}(1-x_2)^{-1}(1-x_3)^{-1}\ldots \times (1-x_j)^{-1}\ldots$$

where the $x_j$'s are a range of related variables satisfying the condition $x_j < 1$ and the product is over a range of values of $j$. Since it is possible to write

$$(1-x_j)^{-1} = 1+x_j+x_j^2+\ldots = \sum_{n=0}^{\infty} x_j^n$$

then

$$\prod_j (1-x_j)^{-1} = \prod_j \left(\sum_{n=0}^{\infty} x_j^n\right) = \left(\sum_{n=0}^{\infty} x_1^n\right)\left(\sum_{n=0}^{\infty} x_2^n\right) \times \left(\sum_{n=0}^{\infty} x_3^n\right)\ldots\left(\sum_{n=0}^{\infty} x_j^n\right)\ldots \qquad 10.40$$

The general term in the product on the right-hand side of equation 10.40 is $x_1^{n_1}x_2^{n_2}x_3^{n_3}\ldots x_j^{n_j}\ldots$ where each of the exponents, $n_1, n_2, \ldots, n_j$, etc., may take any value from 0 to $\infty$. The equation 10.40 may therefore be rewritten as a sum of such general terms so that

$$\prod_j (1-x_j)^{-1} = \sum_{(n_j)} \left(\prod_j x_j^{n_j}\right) \qquad 10.41$$

where the summation is now over all of the possible sets of the exponents $n_1, n_2, n_3, \ldots, n_j, \ldots$.

If the substitution $x_j = e^{(\mu-\epsilon_j)/kT}$ is made in equation 10.41, then it is seen that

$$\prod_j [1-e^{(\mu-\epsilon_j)/kT}]^{-1} = \sum_{(n_j)} \prod_j [e^{(\mu-\epsilon_j)/kT}]^{n_j} \qquad 10.42$$

The product on the right-hand side of equation 10.42 can clearly be replaced by a summation in the exponent since

$$\prod_j [e^{(\mu-\epsilon_j)/kT}]^{n_j} = (e^{(\mu-\epsilon_1)/kT})^{n_1}\cdot(e^{(\mu-\epsilon_2)/kT})^{n_2}\ldots \times (e^{(\mu-\epsilon_j)/kT})^{n_j}\ldots = \exp[\sum_j n_j(\mu-\epsilon_j)/kT]$$

and therefore equation 10.42 may be written

$$\prod_j [1-e^{(\mu-\epsilon_j)/kT}]^{-1} = \sum_{(n_j)} \exp[\sum_j n_j(\mu-\varepsilon_j)/kT] \qquad 10.43$$

Now, in the definition of the grand partition function given in equation 10.27, i.e.

$$\mathcal{Z} = \sum_i W_i \exp[\sum_s n_s(\mu-\varepsilon_s)/kT] \qquad (10.27)$$

the state of the assembly is given by the set of occupation numbers of the sheets, $n_s$. If the state of the assembly is rather defined in terms of the occupation numbers $n_j$ of the individual states of energy $\epsilon_j$ the summation in the exponent of equation 10.27 must be replaced by $\sum_j n_j(\mu-\epsilon_j)/kT$. For an assembly of indistinguishable bosons the weight $W_i$ of the state defined by a given set of the numbers $n_j$ will be unity* and the grand partition function may be written as

$$\mathcal{Z} = \sum_{(n_j)} \exp[\sum_j n_j(\mu-\varepsilon_j)/kT] \qquad 10.44$$

where $\sum_{(n_j)}$ implies the summation over all possible sets of the occupation numbers $n_1, n_2, \ldots, n_j, \ldots$, etc. A comparison between equations 10.43 and 10.44 leads to the identity

$$\boxed{\mathcal{Z} = \prod_j [1-e^{(\mu-\epsilon_j)/kT}]^{-1}} \qquad 10.45$$

The mean number of systems in an open assembly at temperature $T$ has been given by equation 10.23 as

$$\bar{N} = kT\left\{\frac{\partial \log \mathcal{Z}}{\partial \mu}\right\}_{V,T}$$

The value for the Bose–Einstein assembly is thus

$$\bar{N} = kT\frac{\partial}{\partial \mu}\left\{\log \prod_j [1-e^{(\mu-\epsilon_j)/kT}]^{-1}\right\}_{V,T}$$

$$= -kT\sum_j\left\{\frac{\partial}{\partial \mu}\log[1-e^{(\mu-\epsilon_j)/kT}]\right\}_{V,T}$$

* Once the distribution of the bosons among the *individual states* has been specified an interchange of the bosons amongst themselves cannot produce a new, distinguishable arrangement of the assembly.

so that

$$\overline{N} = \sum_j \frac{1}{e^{(\epsilon_j - \mu)/kT} - 1} \qquad 10.46$$

If $\overline{n_j}$ is the mean occupation number of the energy state $\epsilon_j$ then it is possible to write $\overline{N} = \sum_j \overline{n_j}$ so that, on equating the corresponding terms in equation 10.46, the normal Bose–Einstein distribution is given as

$$\overline{n_j} = \frac{1}{e^{(\epsilon_j - \mu)/kT} - 1} \qquad 10.47$$

which is in agreement with equation 4.8 with the substitution of $\mu/kT$ for $\alpha$. (If the chemical potential is zero, as is the case for a photon gas, then equation 10.47 gives the average number of systems in the energy state $j$ as

$$\overline{n_j} = \frac{1}{e^{\epsilon_j/kT} - 1})$$

### THE FERMI–DIRAC GRAND PARTITION FUNCTION

In the case of an assembly composed of fermions, the occupation number of an energy state $j$ can only be 0 or 1 because of the Pauli exclusion principle. The grand partition function of the assembly in equation 10.44 must therefore be replaced by

$$\tilde{\mathcal{Z}} = \sum_{(n_j = 0 \text{ or } 1)} \exp\left[\sum_j n_j(\mu - \epsilon_j)/kT\right] \qquad 10.48$$

where $\sum_{(n_j = 0 \text{ or } 1)}$ indicates that all the possible combinations of the allowed values $n_1 = 0$ or 1, $n_2 = 0$ or $1, \ldots, n_j = 0$ or $1, \ldots$, etc., are included in the summation.

Now consider the product $\prod_j (1 + x_j)$ taken over a range of associated quantities $x_j$. If the terms in this product are grouped in ascending powers then

$$\prod_j (1 + x_j) = 1 + \sum_j x_j + \sum_j \sum_{l>j} x_j x_l + \sum_j \sum_{l>j} \sum_{m>l} x_j x_l x_m + \ldots \qquad 10.49$$

where the summation over $l > j$ is used to avoid the terms $x_k x_l$

and $x_l x_j$ being counted separately. Each of the terms on the right-hand side of equation 10.49 is of the form $\prod_j x_j^{n_j}$ where $n_j$ can take either of the values 0 or 1. Thus $x_j^0 x_l^0 x_m^0 \ldots = 1, x_j^1 x_l^0 x_m^0 \ldots = x_j, x_j^1 x_l^1 x_m^0 \ldots = x_j x_l$ and so forth. Equation 10.49 may thus be rewritten as

$$\prod_j (1+x_j) = \sum_{(n_j = 0 \text{ or } 1)} \prod_j x_j^{n_j} \qquad 10.50$$

where the summation is over all the possible combinations of the exponents $n_j$ allowing for the condition $n_j = 0$ or 1. If the substitution $x_j = e^{(\mu - \epsilon_j)/kT}$ is made in equation 10.50 then it follows that

$$\prod_j [1+e^{(\mu-\epsilon_j)/kT}] = \sum_{(n_j=0 \text{ or } 1)} \prod_j [e^{(\mu-\epsilon_j)/kT}]^{n_j}$$

$$= \sum_{(n_j=0 \text{ or } 1)} \exp[\sum_j n_j(\mu-\epsilon_j)/kT] \qquad \mathbf{10.51}$$

With $\mu$ as the chemical potential and $\epsilon_j$ as the energy of the state $j$ of the systems, a comparison of the equations 10.48 and 10.51 shows that the Fermi–Dirac grand partition function is given by

$$\boxed{\mathcal{Z} = \prod_j [1+e^{(\mu-\epsilon_j)/kT}]} \qquad \mathbf{10.52}$$

The mean number of systems in a Fermi–Dirac assembly is obtained by the application of equation 10.23 which gives

$$\bar{N} = kT\left\{\frac{\partial \log \mathcal{Z}}{\partial \mu}\right\}_{V,T}$$

$$= kT\left\{\frac{\partial}{\partial \mu} \log \prod_j [1+e^{(\mu-\epsilon_j/kT}]\right\}_{V,T}$$

$$= kT \sum_j \left\{\frac{\partial}{\partial \mu} \log[1+e^{(\mu-\epsilon_j)/kT}]\right\}_{V,T}$$

so that

$$\bar{N} = \sum_j \frac{1}{e^{(\epsilon_j - \mu)/kT}+1} \qquad 10.53$$

The normal Fermi–Dirac distribution is obtained on writing $\bar{N} = \sum_j \bar{n}_j$ so that the mean number of systems in the state $j$ is

$$\bar{n}_j = \frac{1}{e^{(\epsilon_j-\mu)/kT}+1} \qquad 10.54$$

in agreement with equation 5.10 with $\mu$ replacing the Fermi energy $\epsilon_F$.

Two points should be noted about the results in this section. First, the average occupation numbers in the Bose–Einstein distribution (equation 10.47) may be greater than one while, because of the Pauli exclusion principle, the average occupation numbers given by equation 10.54 are all fractional. Second, the results in equations 10.37, 10.45 and 10.54 for the three different distributions were all obtained without recourse to any of the approximation methods employed in the "microcanonical" treatments given in Chapters 2 to 5.

## 10.4. *Fluctuations in the number of systems*

As in the case of the mean square deviation of the energy of an assembly (see section 9.7), the mean square deviation of the number of systems in an open assembly may be written as

$$\overline{(\delta N)^2} = \overline{N^2} - \overline{N}^2 \qquad 10.55$$

Now the mean number of systems in the assembly, $\overline{N}$, was given in equation 10.23 as

$$\overline{N} = \sum_i p_i N_i = \sum_i \frac{N_i e^{(\mu N_i - E_i)/kT}}{\mathcal{Z}} = \frac{kT}{\mathcal{Z}}\left\{\frac{\partial \mathcal{Z}}{\partial \mu}\right\}_{V,T} \qquad (10.23)$$

In a similar manner, the mean square number of systems of the assembly may be defined as

$$\overline{N^2} = \sum_i p_i N_i^2 = \sum_i \frac{N_i^2 e^{\mu N_i - E_i/kT}}{\mathcal{Z}} = \frac{(kT)^2}{\mathcal{Z}}\left\{\frac{\partial^2 \mathcal{Z}}{\partial \mu^2}\right\}_{V,T} \qquad 10.56$$

With $\dfrac{\overline{N}}{kT} = \dfrac{1}{\mathcal{Z}}\left\{\dfrac{\partial \mathcal{Z}}{\partial \mu}\right\}_{V,T}$ taken from equation 10.23 and

$$\frac{\overline{N^2}}{(kT)^2} = \frac{1}{\mathcal{Z}}\left\{\frac{\partial^2 \mathcal{Z}}{\partial \mu^2}\right\}_{V,T}$$

from equation 10.56 it is possible to use the identity

$$\frac{\partial}{\partial \mu}\left\{\frac{1}{\mathcal{Z}}\left(\frac{\partial \mathcal{Z}}{\partial \mu}\right)\right\}_{V,T} = \left\{\frac{1}{\mathcal{Z}}\frac{\partial^2 \mathcal{Z}}{\partial \mu^2} - \frac{1}{\mathcal{Z}^2}\left(\frac{\partial \mathcal{Z}}{\partial \mu}\right)^2\right\}_{V,T}$$

to give

$$\frac{1}{(kT)}\left\{\frac{\partial \bar{N}}{\partial \mu}\right\}_{V,T} = \frac{1}{(kT)^2}(\overline{N^2} - \bar{N}^2) \qquad 10.57$$

With the mean square deviation $\overline{(\delta N^2)}$ given by equation 10.55, the equation 10.57 becomes

$$\overline{(\delta N)^2} = kT\left\{\frac{\partial \bar{N}}{\partial \mu}\right\}_{V,T} \qquad 10.58$$

In the case of the semi-classical grand canonical ensemble the mean number of systems in an assembly is given by equation 10.34 as $\bar{N} = Ze^{\mu/kT}$ so that equation 10.58 gives

$$\overline{(\delta N)^2} = kT\left\{\frac{\partial (Ze^{\mu/kT})}{\partial \mu}\right\}_{V,T}$$
$$= Ze^{\mu/kT}$$

or

$$\overline{(\delta N)^2} = \bar{N} \qquad 10.59$$

Now consider a large volume of gas in which some small component volume may be treated as a member assembly in the grand canonical ensemble formed by the whole gas. In such a case the mean square deviation of the number of molecules in the smaller volume will, by equation 10.59, be equal to the mean number of molecules in that volume. Also, if the mean fractional fluctuation of the number of systems is defined as

$$\mathscr{F} = \left\{\frac{\overline{(\delta N)^2}}{\bar{N}^2}\right\}^{\frac{1}{2}} \qquad 10.60$$

then, using equation 10.59, this fluctuation becomes

$$\mathscr{F} = (\bar{N})^{-\frac{1}{2}}$$

This fractional fluctuation is of the same order as the fractional energy fluctuation given in equation 9.49 and is clearly negligible for normally sized volumes of gas. For example, one cubic millimetre of a gas at S.T.P. contains approximately $3 \times 10^{16}$ molecules so that, in this case, $\mathscr{F} \simeq 5 \times 10^{-9}$.

The fluctuations in the Bose–Einstein and Fermi–Dirac ensembles are considered in the exercises at the end of the chapter.

## 10.5. *The chemical potentials in the equilibrium state*

Consider an assembly which is composed of two parts divided by a permeable partition. Such an assembly is shown schematically in Fig. 31 where systems may pass freely from one side of the barrier to the other.

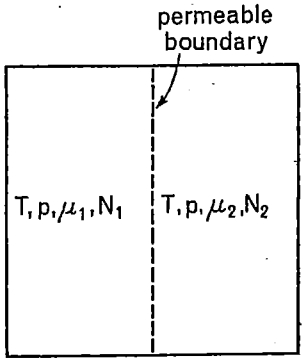


Fig. 31. Assembly divided by a permeable barrier.

Let the temperature and the pressure on the two sides of the barrier be the same but let the chemical potentials of the systems on the two sides be $\mu_1$ and $\mu_2$ and the numbers of systems be $N_1$ and $N_2$ respectively. (The systems are to be considered as being otherwise indistinguishable.)

In order to establish the equilibrium condition of the assembly it is necessary to consider the free energy of the assembly. Since $F = E - TS$, a change in the thermodynamic conditions of the assembly will produce a change in the free energy of

$$dF = dE - T\,dS - S\,dT \tag{10.61}$$

The change in the energy of the assembly is given by equation 10.3 as $dE = T\,dS - p\,dV + \sum_t \mu_t\,dN_t$ so that equation 10.61 may be rewritten as

$$dF = -S\,dT - p\,dV + \sum_t \mu_t\,dN_t \tag{10.62}$$

Where the subscript will here take the values 1 and 2. If the volume and temperature are maintained constant, a change in the number of systems in the two sides of the assembly of Fig. 31 will thus produce a change in the free energy of

$$dF = \mu_1\,dN_1 + \mu_2\,dN_2 \tag{10.63}$$

where $dN_1$ and $dN_2$ are the increases in the numbers of systems on the two sides of the barrier respectively. Now, if the assembly is

closed so that the total number of systems $(N_1+N_2)$ is fixed, the changes in the number of systems must be such that

$$dN_1+dN_2=0$$

or

$$dN_1=-dN_2 \qquad 10.64$$

Substitution from equation 10.64 into equation 10.63 gives

$$dF=(\mu_1-\mu_2)dN_1 \qquad 10.65$$

Clearly, if the assembly is in an equilibrium state, the infinitesimal exchange of systems across the barrier must produce no change in the free energy, since $\partial F/\partial N_1=\partial F/\partial N_2=0$ at equilibrium. The condition for equilibrium obtained from equation 10.65 is thus

$$\mu_1-\mu_2=0$$

or

$$\mu_1=\mu_2 \qquad 10.66$$

It is therefore clear that, if an assembly is to be in an equilibrium state, all three of the intensive variables—temperature, pressure and chemical potential—must be constant throughout the assembly.

This uniformity of the chemical potentials has a particular application to the case of the electron energy levels in metals and semiconductors. Thus, if a comparison is made between the Fermi–Dirac distributions given in equations 10.54 and 5.9, it will be seen that the Fermi energy and the chemical potential are identical for an electron gas. It follows that, in a metal or semiconductor or in a device consisting of a combination of metals and semiconductors, the Fermi level must be constant throughout the materials if they are to be in an equilibrium state.

## PROBLEMS

1. Show that the mean square deviations of the numbers of systems in an assembly obey the following relationships:

(*a*) Bose–Einstein; $\overline{(\delta N)^2}=\sum_i \overline{n_i}(1+\overline{n_i})=\sum_i \overline{(\delta n_i^2)}$

and $\left\{\dfrac{\overline{(\delta n_i)^2}}{\overline{n_i^2}}\right\}=\dfrac{1}{\overline{n_i}}+1$

(*b*) Fermi–Dirac; $\overline{(\delta N)^2} = \sum_i \overline{n_i}(1-\overline{n_i}) = \sum_i \overline{(\delta n_i^2)}$

and $\left\{\frac{\overline{(\delta n_i)^2}}{\overline{n_i^2}}\right\} = \frac{1}{\overline{n_i}} - 1$

2. Considering an assembly of localized systems which are otherwise indistinguishable, show that it will have a grand partition function of the form

$$\mathcal{Z} = \sum_{(n_s)} N! \prod_s \frac{(g_s e^{(\mu-\epsilon_s)/kT})^{n_s}}{n_s!}$$
$$= (1 - Ze^{\mu/kT})^{-1}$$

where $Z = \sum_s g_s e^{-\epsilon_s/kT}$ and, for a given state, $N = \sum_s n_s$.

3. Using equation 10.12 show that the chemical potential of a molecule in a semi-classical perfect gas is

$$-kT \log\left[\frac{V}{N}\left\{\frac{2\pi mkT}{h^2}\right\}^{\frac{3}{2}}\right]$$

4. Using equations 10.21*b* and 10.22 obtain an expression for the entropy in terms of the grand partition function. Compare the result with that of equation 9.13.

# Bibliography

The list of books which is given here may be considered to fall into two groups. First are those introductory texts which will give the student an alternative viewpoint to that which has been presented here. Second are those works which may be of use to those wishing to study the subject of statistical physics beyond an elementary level.

*Elementary*

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# APPENDICES

Appendix 1

# The Lagrange Undetermined Multipliers

If it is required to find the maximum or minimum value of some function $f(x, y, z)$ of the variables $x, y$ and $z$ then it is normally sufficient to solve the equation

$$df = \frac{\partial f}{\partial x}dx + \frac{\partial f}{\partial y}dy + \frac{\partial f}{\partial z}dz = 0 \qquad \text{A1.1}$$

to find the condition that $f$ is stationary for all small changes $dx$, $dy$, $dz$ of the three variables. However, if a condition is imposed on the values which $x$, $y$ and $z$ may take, e.g. $x+y+z =$ constant, say, then it is possible that the stationary point which is defined by equation A1.1 is outside the allowed range of the variables $x$, $y$ and $z$.

Suppose that a general condition, which may be written as

$$\phi(x, y, z) = 0 \qquad \text{A1.2}$$

is imposed on the variables. The solution given by equation A1.1 must now take into account this limitation which restricts the range of the variables $x$, $y$ and $z$ and of $dx$, $dy$ and $dz$. Writing the condition of equation A1.2 in the differential form such that

$$d\phi = \frac{\partial \phi}{\partial x}dx + \frac{\partial \phi}{\partial y}dy + \frac{\partial \phi}{\partial z}dz = 0$$

it follows that one of the increments $dx$, $dy$ or $dz$ can be expressed in terms of the other two. For example, it is possible to write

$$dx = -\left(\frac{\partial \phi}{\partial y}dy + \frac{\partial \phi}{\partial z}dz\right) \Big/ \frac{\partial \phi}{\partial x} \qquad \text{A1.3}$$

Substituting from equation A1.3 into equation A1.1 allows the condition for the maximum or minimum to be written in terms of

$dy$ and $dz$ only so that

$$df = \left[\frac{\partial f}{\partial y} - \frac{\partial f}{\partial x}\left(\frac{\partial \phi/\partial y}{\partial \phi/\partial x}\right)\right] dy + \left[\frac{\partial f}{\partial z} - \frac{\partial f}{\partial x}\left(\frac{\partial \phi/\partial z}{\partial \phi/\partial x}\right)\right] dz = 0 \qquad \text{A1.4}$$

With $\frac{\partial f}{\partial x}\Big/\frac{\partial \phi}{\partial x}$ at the stationary point set equal to $-\alpha$ so that $\left(\frac{\partial f}{\partial x} + \alpha\frac{\partial \phi}{\partial x}\right) = 0$, equation A1.4 may be written as

$$df \equiv \left(\frac{\partial f}{\partial x} + \alpha\frac{\partial \phi}{\partial x}\right) dx + \left(\frac{\partial f}{\partial y} + \alpha\frac{\partial \phi}{\partial y}\right) dy + \left(\frac{\partial f}{\partial z} + \alpha\frac{\partial \phi}{\partial z}\right) dz = 0 \qquad \text{A1.5}$$

For equation A1.5 to define a stationary point it is necessary that each of the brackets shall be identically zero since, as the equation must be satisfied for any values of the increments $dy$ and $dz$, the second and third brackets must be zero while the first bracket is identically zero by the definition of $\alpha$.

Because $\alpha$ is given by the ratio $-\frac{\partial f}{\partial x}\Big/\frac{\partial \phi}{\partial x}$ at the stationary point it can only be found by substitution from the solution of equation A1.5 into the original condition $\phi(x, y, z) = 0$. For this reason $\alpha$ is known as an undetermined multiplier or, more usually, a Lagrange undetermined multiplier.

Once this method is accepted it is possible to express equation A1.5 in the more general total differential form

$$df + \alpha\, d\phi = 0 \qquad \text{A1.6}$$

Also, if the number of variables on which the function $f$ depends and the number of conditions imposed on these variables were increased, an equation similar to A1.6 would still be obtained. Suppose that it is required to find the maximum or minimum of a function $F(x_1, x_2, x_3, \ldots, x_n)$ under the conditions that $\phi_1(x_1, x_2, x_3, \ldots, x_n) = 0$ and $\phi_2(x_1, x_2, x_3, \ldots, x_n) = 0$. An extension of the above argument will show that it is necessary to solve the equation

$$dF + \beta\, d\phi_1 + \gamma\, d\phi_2 = 0 \qquad \text{A1.7}$$

where the Lagrange undetermined multipliers $\beta$ and $\gamma$ are defined

in a manner similar to that for $\alpha$ in equations A1.5 and A1.6. Once the conditional maxima or minima have been found from the equation A1.7 it is possible to find the appropriate values of the multipliers $\beta$ and $\gamma$ by substituting back in the equations $\phi_1 = 0$ and $\phi_2 = 0$.

Appendix 2

# Stirling's Approximation

In order to obtain a simple approximation to the quantity $N!$ it is convenient to use the logarithmic form as

$$\log N! = \log N + \log (N-1) + \ldots + \log 2 + \log 1$$
$$= \sum_{n=1}^{N} \log n \qquad \text{A2.1}$$

This quantity $\log n$ can be represented, for integral values of $n$, by constructing a histogram as shown in Fig. A1. The continuous curve of $\log x$ is superimposed on this histogram and it will be clear that, for large values of $x$ and $n$, the area under the histogram will be very nearly equal to that under the continuous curve. Allowing for the fact that the histogram to $n = N$ will extend to the

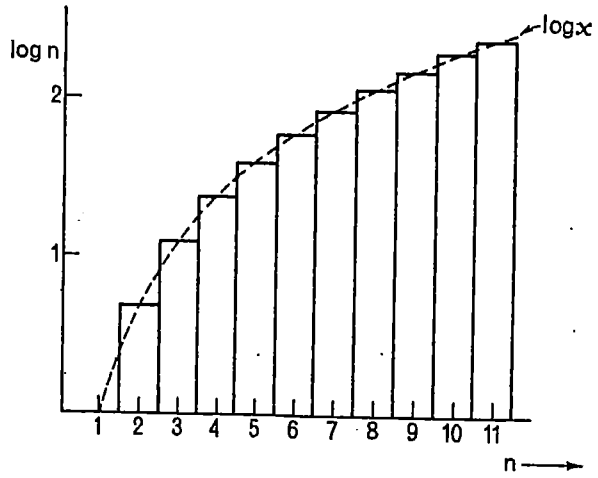


Fig. A1. Histogram of $\log n$ for integral values of $n$ with the continuous curve of $\log x$ superimposed.

point $(N+\frac{1}{2})$, as will be seen from Fig. A1, the two areas may be conveniently equated as

$$\sum_{n=1}^{N} \log n \simeq \tfrac{1}{2} \log N + \int_{1}^{N} \log x \, dx \qquad \text{A2.2}$$

Then, evaluating the integral as $(N \log N - N + 1)$ and substituting from equation A2.1, the approximation

$$\log N! \simeq (N+\tfrac{1}{2}) \log N - N + 1 \qquad \text{A2.3}$$

is obtained.

Stirling has given a more accurate approximation as

$$\log N! \simeq (N+\tfrac{1}{2}) \log N - N + \tfrac{1}{2} \log 2\pi \qquad \text{A2.4}$$

However, at the large values of $N$ with which statistical mechanics is concerned (and also allowing for the fact that it is the differences and the differentials of the terms $\log N!$ which are generally of importance) it is sufficient to reduce the approximations of both equations A2.3 and A2.4 to

$$\log N! \simeq N \log N - N \qquad \text{A2.5}$$

A comparison of the approximations in equations A2.4 and A2.5 is given in the following table from which it will be seen that the fractional error introduced by equation A2.5 is reduced rapidly as $N$ increases.

| $N$ | $\log N!$ | $(N+\frac{1}{2}) \log N - N + \frac{1}{2} \log 2\pi$ | $N \log N - N$ |
|---|---|---|---|
| 10 | 15·1 | 15·1 | 13·0 |
| 20 | 42·3 | 42·3 | 39·9 |
| 50 | 148·5 | 148·5 | 145·4 |

Appendix 3

# Derivation of the Distribution over Energies for a Classical Ensemble

In deriving the distribution of the energies of assemblies within an ensemble use will be made here of the concept of the density of states in phase space. Consider that the state of an assembly within an ensemble may be defined in terms of the $6N$ coordinates of the systems, $x_i, y_i, z_i, p_{xi}, p_{yi}, p_{zi}$ where $i$ may take all values from 1 to $N$. The state of such an assembly may then be represented by a single point in a $6N$-dimensional phase space. Similarly the states of the other assemblies within the ensemble will be represented by other points in phase space.

Now suppose that the density of these representative points in a given region of phase space is $\rho$ so that the number of such points in a volume $d\Gamma_{6N}$ of the phase space is $\rho\, d\Gamma_{6N}$. As time passes, the coordinates representing a given assembly will change and there will be a movement of the points in phase space. However, since the total number of assemblies and therefore the total number of representative points is constant, the density $\rho$ must obey the equation for continuous flow of a fluid, i.e.

$$\frac{\partial \rho}{\partial t} + \operatorname{div}(\rho \mathbf{v}) = 0 \qquad \text{A3.1}$$

where $\mathbf{v}$ is the fluid velocity and $\rho$ is its density at a point in space.

The quantity $\operatorname{div}(\rho\mathbf{v})$ in three dimensions has the form

$$\operatorname{div}(\rho\mathbf{v}) = \frac{\partial}{\partial x}(\rho v_x) + \frac{\partial}{\partial y}(\rho v_y) + \frac{\partial}{\partial z}(\rho v_z)$$

$$= \dot{x}\frac{\partial \rho}{\partial x} + \rho\frac{\partial \dot{x}}{\partial x} + \dot{y}\frac{\partial \rho}{\partial y} + \rho\frac{\partial \dot{y}}{\partial y} + \dot{z}\frac{\partial \rho}{\partial z} + \rho\frac{\partial \dot{z}}{\partial z} \qquad \text{A3.2}a$$

$$= \sum_{x,y,z}\left\{\dot{x}\frac{\partial \rho}{\partial x} + \rho\frac{\partial \dot{x}}{\partial x}\right\} \qquad \text{A3.2}b$$

where $\dot{x}$ is substituted for the $x$-component of velocity $v_x$, etc., and the summation includes all the terms in equation A3.2$a$. For

the $6N$-dimensional phase it is necessary to replace equation A3.2*b* by the more general expression

$$\mathrm{div}_{6N}(\rho \mathbf{v}) = \sum_{i=1}^{N} \sum_{x_i, y_i, z_i} \left\{ \dot{x}_i \frac{\partial \rho}{\partial x_i} + \rho \frac{\partial \dot{x}_i}{\partial x_i} + \dot{p}_{xi} \frac{\partial \rho}{\partial p_{xi}} + \rho \frac{\partial \dot{p}_{xi}}{\partial p_{xi}} \right\} \tag{A3.3}$$

with each of the coordinates $x_i$, $y_i$, $z_i$, $p_{xi}$, $p_{yi}$, $p_{zi}$ treated equally as linear dimensions in phase space.

This equation A3.3 may be simplified by considering the energy of the system $i$ to be expressed in the Hamiltonian form

$$H_i = \frac{p_{xi}^2}{2m} + \frac{p_{yi}^2}{2m} + \frac{p_{zi}^2}{2m} + V(x_i, y_i, z_i) \tag{A3.4}$$

where $V(x_i, y_i, z_i)$ is the potential energy of the system $i$ as a function of its spatial coordinates. From equation A3.4 it is possible to obtain the partial differentials

$$\frac{\partial H_i}{\partial p_{xi}} = \frac{p_{xi}}{m} = v_{xi} = \dot{x}_i \tag{A3.5}$$

and

$$\frac{\partial H_i}{\partial x_i} = \frac{\partial V}{\partial x_i} \tag{A3.6}$$

Now the negative rate of change of the potential energy, $-\dfrac{\partial V}{\partial x_i}$, represents the force in the direction $x_i$ and hence is equal to the rate of change of the momentum $p_{xi}$. Thus, equation A3.6 becomes

$$\frac{\partial H_i}{\partial x_i} = \frac{\partial V}{\partial x_i} = -\dot{p}_{xi} \tag{A3.7}$$

By taking the second differentials of equations A3.5 and A3.7 it is possible to obtain

$$\frac{\partial}{\partial x_i}\left\{\frac{\partial H_i}{\partial p_{xi}}\right\} = \frac{\partial \dot{x}_i}{\partial x_i} \tag{A3.8}$$

and

$$\frac{\partial}{\partial p_{xi}}\left\{\frac{\partial H_i}{\partial x_i}\right\} = -\frac{\partial \dot{p}_{xi}}{\partial p_{xi}} \tag{A3.9}$$

The differentials on the left-hand sides of equations A3.8 and A3.9 are identical so that

$$\frac{\partial \dot{x}_i}{\partial x_i} = -\frac{\partial \dot{p}_{xi}}{\partial p_{xi}} \qquad \text{A3.10}$$

Substitution from equation A3.10 into equation A3.3 gives, on cancellation,

$$\mathrm{div}_{6N}(\rho \mathbf{v}) = \sum_{i=1}^{N} \sum_{x_i, y_i, z_i} \left\{ \dot{x}_i \frac{\partial \rho}{\partial x_i} + \dot{p}_{xi} \frac{\partial \rho}{\partial p_{xi}} \right\} \qquad \text{A3.11}$$

and the equation of continuity, A3.1, is simplified to

$$\frac{\partial \rho}{\partial t} + \sum_{i=1}^{N} \sum_{x_i, y_i, z_i} \left\{ \dot{x}_i \frac{\partial \rho}{\partial x_i} + \dot{p}_{xi} \frac{\partial \rho}{\partial p_{xi}} \right\} = 0 \qquad \text{A3.12}$$

Since $\dot{x}_i = \dfrac{dx_i}{dt}$ and $\dot{p}_{xi} = \dfrac{dp_{xi}}{dt}$ the left-hand side of equation A3.12 A3.12 is, by definition, the total differential $\dfrac{d\rho}{dt}$ so that the continuity equation becomes the normal Liouville condition

$$\frac{d\rho}{dt} = 0 \qquad \text{A3.13}$$

*Thus the density in phase space, of the points which represent the assemblies, is a constant in time* and this density must therefore be a function of the constants of the motion of the assembly only. Those properties of the assembly which are constant with time may be taken as the total energy $E$, the number of systems $N$, the total linear momentum and the total angular momentum. The latter two quantities will necessarily be zero in a normal static assembly so that it is possible to write

$$\rho = f(E, N) \qquad \text{A3.14}$$

Now consider two assemblies having energies $E_1$ and $E_2$ and numbers of systems $N_1$ and $N_2$ respectively. Let the state of the first assembly be represented by a point in $6N_1$-dimensional phase space in a region where the density of points is $\rho_1$. Similarly, let the second system be in a $6N_2$-dimensional phase space with a density $\rho_2$. If the state of the two assemblies together is represented by a point in a $6(N_1 + N_2)$-dimensional phase space then, since the density of points in a given region is proportional to the

probability of finding the assembly in a given state, the density of points in the neighbourhood of this combined state will clearly be proportional to the product of the densities $\rho_1$ and $\rho_2$. If this density for the two assemblies together is $\rho_T$ and if $E_T$ and $N_T$ are the total energies and total number of systems respectively, it follows that

$$E_1+E_2 = E_T \qquad \textbf{A3.15}a$$

$$N_1+N_2 = N_T \qquad \textbf{A3.15}b$$

and

$$\rho_1\rho_2 \propto \rho_T \qquad \text{A3.15}c$$

When the equations A3.15 are taken together with equation A3.14 it is seen that the expression for the density of states must satisfy a relation of the form

$$f(E_1, N_1)f(E_2, N_2) \propto f(E_1+E_2, N_1+N_2)$$

The solution of this equation for all values of $E$ and $N$ is obtained by writing

$$\log f(E, N) = a+bE+cN$$

The density of states is thus given by

$$\log \rho = a+bE+cN \qquad \text{A3.16}$$

which satisfies the equations A3.15 simultaneously provided that $a$, $b$ and $c$ are independent of $E$ and $N$.

The application of equation A3.16 to the three types of ensembles discussed in the text yields the following results.

(i) THE MICROCANONICAL ENSEMBLE

In the microcanonical ensemble both the energy $E$ and the number of systems, $N$, of each assembly is fixed.* (The condition on the energy is usually defined more reasonably by taking its value between the energies $E$ and $E+\delta E$ where $\delta E$ is an infinitesimal increment. Under this condition all the allowed points in phase space lie in a shell the size of which is determined by the size of $\delta E$. If $\delta E$ is taken as zero then all the allowed points will lie on a surface in phase space.) The density in phase space in this case may then be written

$$\rho = \text{constant} \qquad \text{A3.17}$$

* See footnote p. 129.

It follows that the points in phase space can only move over the infinitesimal shell defined by the almost constant energy of the assemblies and the density of the points within the shell will remain constant. This result, it should be noted, says nothing about the distribution of the energies of the individual systems within the assembly.

(ii) THE CANONICAL ENSEMBLE

With the number of systems of an assembly in the canonical ensemble as a fixed quantity the density of the points in phase space is given by equation A3.16 as

$$\log \rho = bE + \text{constant} \qquad \text{A3.18}$$

As the probability $p_i$ of finding an assembly in the energy state $E_i$ will be directly proportional to the appropriate density $\rho$ then $\log p_i$ will be linearly dependent on $E_i$ and it follows that

$$p_i = e^{(\psi - E_i)/\theta} \qquad \text{A3.19}$$

where $\psi$ and $\theta$ are constants for the ensemble and the negative sign for $E_i$ is chosen since $p_i$ will decrease as $E_i$ increases. (Comparison of equation A3.19 with equation 9.12 shows that $\theta$ must be equated to the quantity $kT$ and that $\psi$ is the free energy $F$.)

(iii) THE GRAND CANONICAL ENSEMBLE

For the grand canonical ensemble both $E$ and $N$ must be considered as variables in equation A3.16 so that, with the probability $p_i$ again taken proportional to $\rho$, it follows that

$$p_i = e^{(\chi + \xi N_i - E_i)/\theta} \qquad \text{A3.20}$$

where $E_i$ and $N_i$ are the energy and the number of systems for the state $i$ respectively. Again $\theta \equiv kT$ and comparison with equation 10.13 shows that $\xi$ is the chemical potential and $\chi$ is the grand potential $(-pV)$.

(Two points in the proof of equation A3.13 are of particular interest. Firstly, the same result would be obtained with any set of conjugate coordinates and momenta, not just with the linear coordinates taken here (see the footnote p. 3). Secondly, the invariance of the density in phase space and its independence of the particular coordinate system chosen explains the usefulness of the representation of the assemblies by points in this particular space.)

Appendix 4

# Equivalent Volumes in Phase Space

In section 1.2 an element $d\Gamma$ of a six-dimensional phase space was defined by the relation

$$d\Gamma = dxdydzdp_x dp_y dp_z \tag{1.1}$$

As an extension of this definition it is useful to consider the volumes of phase space in different representations.

Consider first the volume of momentum space lying between the two values of the total momentum $p$ and $p+dp$. If the total momentum is expressed in polar coordinates $(p, \theta, \phi)$ then the element of momentum space with coordinates in the range $p$ to $p+dp$, $\theta$ to $\theta+d\theta$ and $\phi$ to $\phi+d\phi$ is seen from Fig. A2 to be

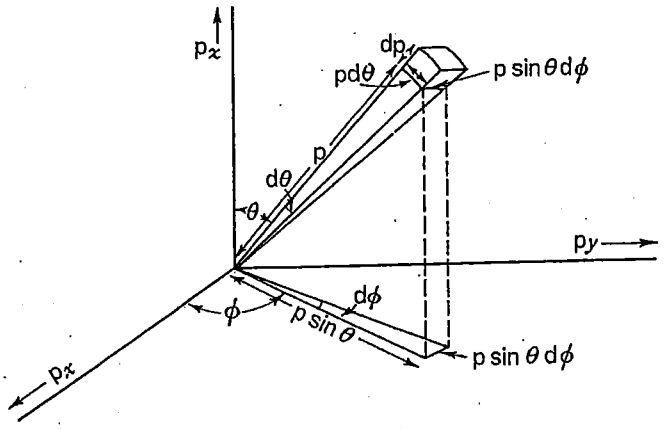


Fig. A2. Element of volume of momentum space shown in polar coordinates.

$$dV_p = dp \,.\, p\, d\theta \,.\, p \sin\theta d\phi = p^2 \sin\theta d\theta d\phi dp \tag{A4.1}$$

The corresponding volume of phase space for which the position coordinates are in the range $x$ to $x+dx$, $y$ to $y+dy$ and $z$ to $z+dz$ is thus

$$d\Gamma = dxdydz \,.\, p^2 \sin\theta d\theta d\phi dp \tag{A4.2}$$

The volume of momentum space $\Delta V_p$ lying between $p$ and $p+dp$ and independent of the direction is obtained by integrating equation A4.1 over all values of the angles $0$ and $\phi$. That is

$$\Delta V_p = p^2\,dp\int_0^{\pi}\sin 0\,d0\int_0^{2\pi}d\phi$$

$$= 4\pi p^2\,dp \qquad \text{A4.3}$$

which is, of course, simply the volume of the spherical shell between $p$ and $p+dp$.

The volume of phase space $\Delta\Gamma$ corresponding to the volume $\Delta V_p$ in momentum space and the volume $V$ in ordinary space is now given by

$$\Delta\Gamma = 4\pi p^2\,dp\int_V dxdydz$$

or

$$\boxed{\Delta\Gamma = 4\pi p^2\,dp\,.\,V} \qquad \text{A4.4}$$

From equation 1.1 it is possible to write the volume of phase space corresponding to a range of velocities $v_x$ to $v_x+dv_x$, $v_y$ to $v_y+dv_y$, $v_z$ to $v_z+dv_z$ as

$$d\Gamma = dxdydz\,.\,m^3\,dv_xdv_ydv_z \qquad \text{A4.5}$$

since $p_x = mv_x$, etc. Then by the same substitution for the total velocity, i.e. $p = mv$, equation A4.4 gives, for the volume of phase space with ordinary volume $V$ and total velocity in the range $v$ to $v+dv$,

$$\boxed{\Delta\Gamma = m^3\,.\,4\pi v^2\,dv\,.\,V} \qquad \text{A4.6}$$

Finally consider the element of phase space defined by the kinetic energy interval $\epsilon$ to $\epsilon+d\epsilon$. Since the momentum can be written $p = (2m\epsilon)^{\frac{1}{2}}$ so that $dp = (m/2\epsilon)^{\frac{1}{2}}\,.\,d\epsilon$, equation A4.4 may be written

$$\Delta\Gamma = 4\pi\,.\,2m\epsilon(m/2\epsilon)^{\frac{1}{2}}\,d\epsilon\,.\,V$$

or

$$\boxed{\Delta\Gamma = 2\pi(2m)^{\frac{3}{2}}\epsilon^{\frac{1}{2}}\,d\epsilon\,.\,V} \qquad \text{A4.7}$$

Appendix 5

# The Volume of a State in Phase Space

If a quantum mechanical system is moving with kinetic energy $E$ then the wave motion associated with the system must satisfy the time-independent Schrödinger wave equation

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2 mE}{h^2}\psi = 0 \qquad \text{A5.1}$$

where $h$ is Planck's constant, $m$ is the mass of the system and the wave-function $\psi$ depends on the coordinates $x$, $y$ and $z$ of the system. When the system is moving in free space the solution of equation A5.1 is of the form

$$\psi = \psi_0 e^{j(k_x x + k_y y + k_z z)} \qquad \text{A5.2}$$

where the propagation constants are given by $k_x = 2\pi/\lambda_x = 2\pi p_x/h$, etc., $\lambda_x$ being the wave-length appropriate to the $x$-direction and the components of momentum $p_x$, $p_y$ and $p_z$ must satisfy the condition $(p_x^2+p_y^2+p_z^2) = 2mE$. When, however, the system is enclosed in some limited volume, the wave-functions given by equation A5.2 must satisfy the boundary conditions imposed by the walls of the enclosure.

Consider that the systems described by equation A5.1 are contained in a rectangular box with the sides of length $L_x$, $L_y$ and $L_z$ in the directions of the three axes respectively as shown in Fig. A3. The boundary conditions are most easily included in the solution $\psi$ by considering the wave functions to represent standing waves such that there is a whole number of half-wavelengths in each of the three directions. Then

$$\left.\begin{aligned} n_x\frac{\lambda_x}{2} &= L_x \\ n_y\frac{\lambda_y}{2} &= L_y \\ n_z\frac{\lambda_z}{2} &= L_z \end{aligned}\right\} \qquad \text{A5.3}$$

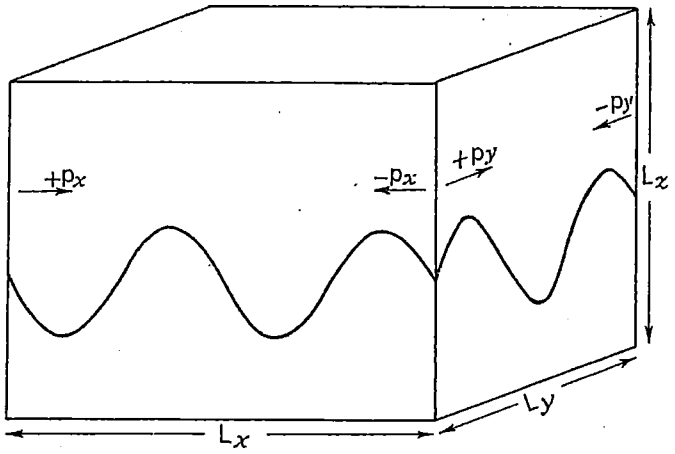


Fig. A3. Wave forms of a system contained in a box.

where $n_x$, $n_y$ and $n_z$ are integers and $\lambda_x$, $\lambda_y$, $\lambda_z$ are the wave-lengths appropriate to the respective directions. In terms of these wave-lengths, given as $\lambda_x = 2L_x/n_x$, etc., the allowed wave-functions in equation A5.2 become, with $k_x = 2\pi/\lambda_x$ etc.,

$$\psi = \psi_0 e^{j\pi(n_x.x/L_x + n_y.y/L_y + n_z.z/L_z)} \qquad \text{A5.4}$$

Since $\lambda_x = h/p_x$, etc., the numbers of half-wavelengths given in equation A5.3 may be expressed in terms of the momentum components as

$$n_x = \frac{2L_x p_x}{h} \qquad \text{A5.5}$$

etc., where it must be remembered that it requires both of the travelling waves, one with momentum $p_x$ and one with momentum $-p_x$, to produce the corresponding standing wave.

If the allowed momentum $p_x$ is increased to $p_x + dp_x$ the number of half-wavelengths in the length $L_x$ is increased to

$$(n_x + dn_x) = \frac{2L_x(p_x + dp_x)}{h}$$

and the number $dn_x$ in this expression will correspond to the number of allowed standing waves having an $x$-direction component of momentum in the range $|dp_x|$.* That is,

$$dn_x = \frac{2L_x\, dp_x}{h} \qquad \text{A5.6}a$$

* The symbol $|dp_x|$ here indicates that the standing waves result from travelling waves having momentum in the range $p_x$ to $p_x + dp_x$ *and* $-p_x$ to $-(p_x + dp_x)$.

Similarly there will be a number of allowed standing waves in the $y$- and $z$-directions, corresponding to the momentum ranges $|dp_y|$ and $|dp_z|$, given by

$$dn_y = \frac{2L_y\,dp_y}{h} \qquad \text{A5.6}b$$

$$dn_z = \frac{2L_z\,dp_z}{h} \qquad \text{A5.6}c$$

Since a state corresponding to a standing wave along one axis may be taken together with any other standing wave in either of the other directions, the total number of standing waves for the volume $L_xL_yL_z$ having momentum components in the range $|dp_x|$, $|dp_y|$ and $|dp_z|$ is

$$dn_s = dn_x dn_y dn_z$$

$$= \frac{8L_xL_yL_z\,dp_x dp_y dp_z}{h^3}$$

However, because each standing wave in a given direction is made up of two allowed momentum states ($p_x$ and $-p_x$, etc.) the actual number of allowed states $d\mathcal{n}$ having momentum components in the range $+dp_x$, $+dp_y$ and $+dp_z$ is one-eighth of this value. That is

$$d\mathcal{n} = \frac{L_xL_yL_z\,dp_x dp_y dp_z}{h^3} \qquad \text{A5.7}$$

In equation A5.7 the quantity $(L_xL_yL_z\,dp_x dp_y dp_z)$ is an element of volume in phase space and it therefore follows that the volume per state in phase space can be identified as $h^3$. (If the rectangular box were taken to have sides $dx, dy, dz$ then equation A5.7 would give the number of states in the infinitesimal volume of phase space $d\Gamma = dxdydzdp_xdp_ydp_z$.)

Taking $L_xL_yL_z$ as the volume $V$ and the total momentum in the range $p$ to $p+dp$ gives a volume of phase space $V.4\pi p^2\,dp$ (see Appendix 4) and the number of allowed states in this volume is

$$d\mathcal{n} = \frac{V.4\pi p^2\,dp}{h^3} \qquad \text{A5.8}$$

Similarly for any general volume of phase space $\Delta\Gamma$ the number of

allowed states may be written

$$\boxed{d\mathscr{n} = \frac{\Delta\Gamma}{h^3}} \qquad \text{A5.9}$$

In terms of the total wave-length $\lambda = h/p$ equation A5.8 gives the number of allowed wave modes with wave-lengths in the range $\lambda$ to $\lambda + d\lambda$ as

$$\boxed{d\mathscr{n} = g(\lambda)\, d\lambda = \frac{4\pi}{\lambda^4} d\lambda} \qquad \text{A5.10}$$

for a unit volume. This expression A5.10 will, of course, hold for acoustic and electromagnetic waves as well as for the de Broglie waves discussed here.

An extension of the above argument to a $6N$-dimensional phase space defined by the coordinates and momentum components of the $N$-systems in an assembly shows that, in this space, the volume per state of the assembly is $(h^3)^N$ and the number of states in an element of phase space $d\Gamma_{6N}$ is

$$d\mathscr{n} = \frac{d\Gamma_{6N}}{h^{3N}} \qquad \text{A5.11}$$

(An alternative derivation of equations A5.7 to A5.10 is obtained by noting that the energy of a system with the wave-function given in equation A5.4 is

$$E = \left\{\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right\}\frac{h^2}{8m} \qquad \text{A5.12}$$

$$= \frac{p_x^2 + p_y^2 + p_z^2}{2m}$$

The number of allowed states in a given momentum range is then found from the possible combinations of the integers $n_x$, $n_y$, $n_z$ within this range. This method is given in some detail in Glasstone, S.: *Theoretical Chemistry*, D. Van Nostrand Co. Inc. 1947.)

Appendix 6

# The Γ-Integrals

In dealing with the Maxwell–Boltzmann distributions for the energies, momenta and velocities of the systems in a classical assembly, and also in dealing with other exponential distributions, it is useful to be able to evaluate certain Γ-integrals defined for positive values of $n$ as

$$\Gamma(n+1) = \int_0^\infty e^{-x}x^n\,dx \qquad \text{A6.1}$$

If partial integration is applied to equation A6.1 then

$$\Gamma(n+1) = -\int_0^\infty x^n\,d(e^{-x})$$

$$= -\left[x^n e^{-x}\right]_0^\infty + n\int_0^\infty e^{-x}x^{n-1}\,dx$$

or, since $\left[x^n e^{-x}\right]_0^\infty = 0$,

$$\Gamma(n+1) = n\Gamma(n) \qquad \text{A6.2}$$

From equation A6.2 it follows that $\Gamma(n) = (n-1)\Gamma(n-1)$ and so on and, therefore, successive integration by parts will give

$$\Gamma(n+1) = n(n-1)(n-2)\ldots(n-s)\Gamma(n-s) \qquad \text{A6.3}$$

From this result it is clear that $\Gamma(n+1)$ has the form of a generalized factorial for $n$.

Two particular solutions of equation A6.3 are of interest. Firstly, if $n$ is an integer and $s = n-1$, then

$$\Gamma(n+1) = n!\,\Gamma(1)$$

$$= n!\int_0^\infty e^{-x}\,dx$$

$$= n! \qquad \text{A6.4}$$

Secondly, if $n$ is half-integral, equation A6.3 gives

$$\Gamma(n+1) = n(n-1)\ldots\frac{3}{2}\cdot\frac{1}{2}\Gamma(\tfrac{1}{2}) \qquad \text{A6.5}$$

with

$$\Gamma(\tfrac{1}{2}) = \int_0^\infty e^{-x}x^{-\frac{1}{2}}\,dx$$

Writing $x^{\frac{1}{2}} = y$ and $dy^2 = 2y\,dy$, then

$$\Gamma(\tfrac{1}{2}) = 2\int_0^\infty e^{-y^2}\,dy = \int_{-\infty}^\infty e^{-y^2}\,dy$$
$$= \sqrt{\pi} \qquad \text{A6.6}$$

(The integral for $\Gamma(\frac{1}{2})$ may be evaluated by writing

$$[\Gamma(\tfrac{1}{2})]^2 = \int_{-\infty}^\infty e^{-y^2}\,dy\int_{-\infty}^\infty e^{-z^2}\,dz$$
$$\equiv \int_{-\infty}^\infty\int_{-\infty}^\infty e^{-(y^2+z^2)}\,dydz \qquad \text{A6.7}$$

Putting $y$ and $z$ in polar form so that $y = r\cos\theta$, $z = r\sin\theta$, $y^2+z^2 = r^2$ and $dydz \equiv r\,drd\theta$ the integral in equation A6.7 becomes

$$[\Gamma(\tfrac{1}{2})]^2 = \int_0^{2\pi}\int_0^\infty e^{-r^2}r\,drd\theta \qquad \text{A6.8}$$

where the limits of integration are chosen to cover the whole of the $yz$-plane as they did in equation A6.7. Evaluating the integral in equation A6.8 by writing $r\,dr = \frac{1}{2}d(r^2)$ gives

$$[\Gamma(\tfrac{1}{2})]^2 = \tfrac{1}{2}\int_0^{2\pi} d\theta\int_0^\infty e^{-(r^2)}\,d(r^2)$$
$$= \pi$$

and

$$\Gamma(\tfrac{1}{2}) = \sqrt{\pi}.)$$

Equation A6.5 for half-integral values of $n$ then becomes

$$\Gamma(n+1) = n(n-1)\ldots\frac{3}{2}\cdot\frac{1}{2}\cdot\sqrt{\pi} \qquad \text{A6.9}$$

If the $\Gamma$-integral has the modified form in which $e^{-x}$ is replaced

by $e^{-\lambda x}$ then

$$\int_0^\infty e^{-\lambda x} x^n \, dx = \frac{1}{\lambda^{n+1}} \int_0^\infty e^{-\lambda x} (\lambda x)^n \, d(\lambda x)$$

$$= \frac{1}{\lambda^{n+1}} \Gamma(n+1) \qquad \text{A6.10}$$

In particular

$$\int_0^\infty e^{-\lambda x} x^{-\frac{1}{2}} \, dx \equiv \int_0^\infty e^{-\lambda y^2} \, dy = \frac{1}{\lambda^{\frac{1}{2}}} \Gamma(\tfrac{1}{2}) = \sqrt{\frac{\pi}{\lambda}} \qquad \text{A6.11}$$

Finally it is of interest to consider those integrals of the form $\int_0^\infty x^n e^{-ax^2} \, dx$. This integral reduces to a Γ-integral form on writing $y = ax^2$ so that

$$\int_0^\infty x^n e^{-ax^2} \, dx = \frac{1}{2a^{(n+1)/2}} \int_0^\infty y^{(n-1)/2} e^{-y} \, dy$$

$$= \frac{1}{2a^{(n+1)/2}} \Gamma\left(\frac{n+1}{2}\right) \qquad \text{A6.12}$$

Appendix 7

# Integrals Involving the Fermi Function

In studying the properties of an electron gas it is frequently necessary to evaluate integrals involving the Fermi function as defined by equation 5.10, i.e.

$$f(\epsilon) = \frac{1}{e^{(\epsilon - \epsilon_F)/kT} + 1}$$

Since, in all practical cases, the temperature is small compared with the Fermi temperature of the electron gas, the differential of the Fermi function, $f'(\epsilon)$, will be negligible except in the neighbourhood of the Fermi energy $\epsilon_F$. The forms of $f(\epsilon)$ and $f'(\epsilon)$ are shown in Fig. A4 as functions of the energy $\epsilon$.

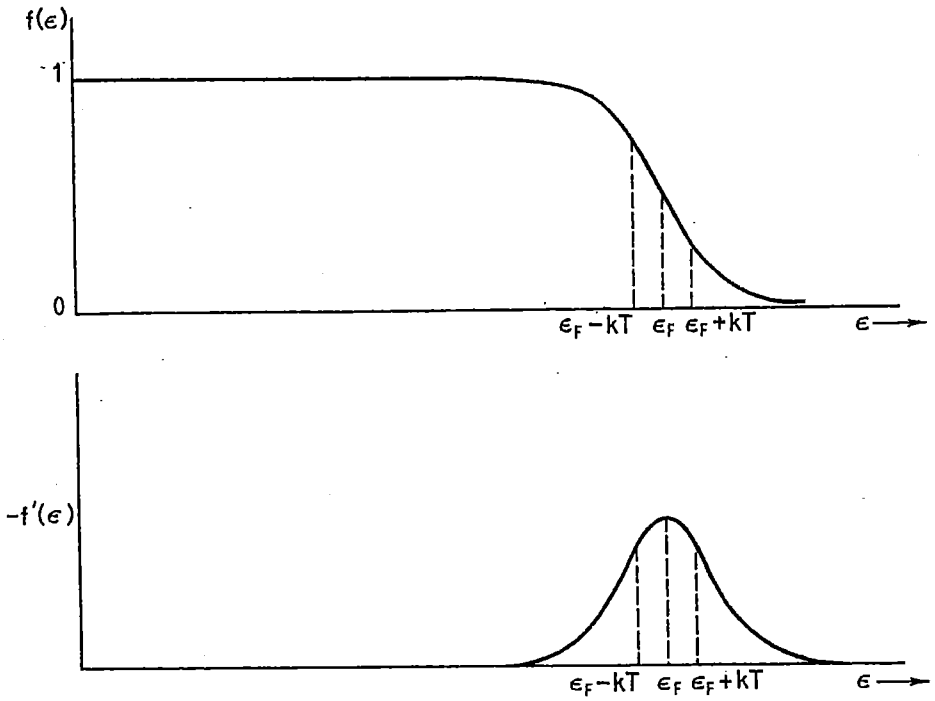


Fig. A4. The Fermi function and its differential with respect to the energy.

Because of the form of $f'(\epsilon)$ it is possible to evaluate many integrals involving $f(\epsilon)$ in the following manner:

Let the integral required be of the form

$$I = \int_0^\infty f(\epsilon)\phi(\epsilon)\,d\epsilon \qquad \text{A7.1}$$

This may be integrated by parts if a function $\Phi(\epsilon)$ is defined as

$$\Phi(\epsilon) = \int_0^\epsilon \phi(\epsilon)\,d\epsilon \qquad \text{or} \qquad d\Phi(\epsilon) = \phi(\epsilon)\,d\epsilon$$

Then equation A7.1 becomes

$$\begin{aligned} I &= \int_0^\infty f(\epsilon)\,d\Phi(\epsilon) \\ &= \Big[f(\epsilon)\Phi(\epsilon)\Big]_0^\infty - \int_0^\infty \Phi(\epsilon)f'(\epsilon)\,d\epsilon \end{aligned} \qquad \text{A7.2}$$

Now $f(\infty) = 0$ and $\Phi(0) = \int_0^0 \phi(\epsilon)\,d\epsilon = 0$ so that $\Big[f(\epsilon)\Phi(\epsilon)\Big]_0^\infty = 0$ and

$$I = -\int_0^\infty \Phi(\epsilon)f'(\epsilon)\,d\epsilon \qquad \text{A7.3}$$

Since $f'(\epsilon)$ is only significantly different from zero in the neighbourhood of $\epsilon = \epsilon_F$ it is sufficient for the present purposes if $\Phi(\epsilon)$ is expanded as a Taylor series about $\epsilon_F$. Taking only the first three terms of the expansion to be significant because of the small range of energies $(\epsilon - \epsilon_F)$ which are of interest, the expansion is

$$\Phi(\epsilon) = \Phi(\epsilon_F) + \Phi'(\epsilon_F)(\epsilon - \epsilon_F) + \Phi''(\epsilon_F)\frac{(\epsilon - \epsilon_F)^2}{2} \qquad \text{A7.4}$$

Equation A7.3 then becomes

$$\begin{aligned} I = &-\Phi(\epsilon_F)\int_0^\infty f'(\epsilon)\,d\epsilon - \Phi'(\epsilon_F)\int_0^\infty f'(\epsilon)(\epsilon - \epsilon_F)\,d\epsilon \\ &-\tfrac{1}{2}\Phi''(\epsilon_F)\int_0^\infty f'(\epsilon)(\epsilon - \epsilon_F)^2\,d\epsilon \end{aligned} \qquad \text{A7.5}$$

Now

$$\int_0^\infty f'(\epsilon)\,d\epsilon = \Big[f(\epsilon)\Big]_0^\infty = -\frac{1}{e^{-\epsilon_F/kT}+1}$$

and, since $\epsilon_F \gg kT$, $e^{-\epsilon_F/kT} \ll 1$ and $\int_0^\infty f'(\epsilon)\,d\epsilon = -1$ (to very good

approximation) so that the first term of the integral given by equation A7.5 is

$$-\Phi(\epsilon_F)\int_0^\infty f'(\epsilon)\,d\epsilon = \Phi(\epsilon_F) = \int_0^{\epsilon_F}\phi(\epsilon)\,d\epsilon \qquad \text{A7.6}$$

The second term in the integral may be evaluated since

$$f'(\epsilon) = -\frac{1}{kT}\frac{e^{(\epsilon-\epsilon_F)/kT}}{[e^{(\epsilon-\epsilon_F)/kT}+1]^2} \qquad \text{A7.7}$$

so that

$$\int_0^\infty f'(\epsilon)(\epsilon-\epsilon_F)\,d\epsilon = -\frac{1}{kT}\int_0^\infty \frac{e^{(\epsilon-\epsilon_F)/kT}(\epsilon-\epsilon_F)}{[e^{(\epsilon-\epsilon_F/kT}+1]^2}\,d(\epsilon-\epsilon_F)$$

$$\equiv -kT\int_{-\epsilon_F/kT}^\infty \frac{xe^x}{(e^x+1)^2}dx \qquad \text{A7.8}$$

when the change of variable to $x = (\epsilon-\epsilon_F)/kT$ is made. Because $\epsilon_F \gg kT$ and $e^{-x}$ goes rapidly to zero as $x$ increases the integral in equation A7.8 may be written, with sufficient accuracy, as an integral from $-\infty$ to $+\infty$. Then

$$\int_0^\infty f'(\epsilon)(\epsilon-\epsilon_F)\,d\epsilon \equiv -kT\int_{-\infty}^\infty \frac{xe^x}{(e^x+1)^2}dx \qquad \text{A7.9}$$

The integrand on the right of this equation is an odd function of $x$ since

$$\left\{\frac{xe^x}{(e^x+1)^2}\right\} = -\left\{\frac{(-x)e^{-x}}{(e^{-x}+1)^2}\right\}$$

and the integral is therefore identically zero. It follows that the second term in equation A7.5 is zero; i.e.

$$-\Phi'(\epsilon_F)\int_0^\infty f'(\epsilon)(\epsilon-\epsilon_F)\,d\epsilon = 0 \qquad \text{A7.10}$$

The evaluation of the third term in equation A7.5 follows a form similar to that for the second term. Thus, using equation A7.7,

$$\int_0^\infty f'(\epsilon)(\epsilon-\epsilon_F)^2 d\epsilon \equiv -(kT)^2\int_{-\infty}^\infty \frac{x^2e^x}{(e^x+1)^2}dx \qquad \text{A7.11}$$

where the substitution $x = (\epsilon-\epsilon_F)/kT$ has again been made and

the lower limit of integration $(-\epsilon_F/kT)$ is taken as $-\infty$. The integrand in equation A7.11 is an even function of $x$ so that

$$\int_{-\infty}^{\infty} \frac{x^2 e^x}{(e^x+1)^2} dx = 2\int_0^{\infty} \frac{x^2 e^x}{(e^x+1)^2} dx$$

$$= 2\int_0^{\infty} \frac{x^2 e^{-x}}{(e^{-x}+1)^2} dx \qquad \text{A7.12}$$

This latter integral may be expanded as an infinite series in $e^{-x}$ by writing

$$(1+e^{-x})^{-2} = \sum_{n=1}^{\infty} (-1)^{n-1} n e^{-(n-1)x}$$

where $n$ is an integer, so that

$$\int_0^{\infty} \frac{x^2 e^{-x}}{(e^{-x}+1)^2} dx = \sum_{n=1}^{\infty} (-1)^{n-1} n \int_0^{\infty} e^{-nx} x^2 \, dx \qquad \text{A7.13}$$

Using the form of the $\Gamma$-integral in equation A6.10 gives

$$\int_0^{\infty} e^{-nx} x^2 \, dx = \frac{1}{n^3}\Gamma(3) = \frac{2}{n^3}$$

so that equation A7.13 becomes

$$\int_0^{\infty} \frac{x^2 e^{-x}}{(e^{-x}+1)^2} dx = 2\sum_{n=1}^{\infty} (-1)^{n-1} \frac{1}{n^2}$$

$$\equiv \sum_{n=1}^{\infty} \frac{1}{n^2} = \frac{\pi^2}{6} \qquad \text{A7.14}$$

Substituting from equation A7.14 into equation A7.12 and then into equation A7.11 gives

$$\int_0^{\infty} f'(\epsilon)(\epsilon-\epsilon_F)^2 \, d\epsilon = -(kT)^2 \frac{\pi^2}{3} \qquad \text{A7.15}$$

From the definition of $\Phi(\epsilon)$, the second differential of this function at the Fermi energy is $\Phi''(\epsilon_F) = \phi'(\epsilon_F)$. The third term in the integral $I$ is thus

$$-\tfrac{1}{2}\Phi''(\epsilon_F)\int_0^{\infty} f'(\epsilon)(\epsilon-\epsilon_F)^2 \, d\epsilon = \phi'(\epsilon_F)(kT)^2 \frac{\pi^2}{6} \qquad \text{A7.16}$$

Substituting from equations A7.16, A7.10 and A7.6 in equation A7.5 gives

$$I = \int_0^\infty f(\epsilon)\phi(\epsilon)\,d\epsilon = \int_0^{\epsilon_F} \phi(\epsilon)\,d\epsilon + \phi'(\epsilon_F)(kT)^2\frac{\pi^2}{6}$$

A7.17

This equation will hold for any function $\phi(\epsilon)$ for which the integral $\int_0^\epsilon \phi(\epsilon)\,d\epsilon$ may be expanded in the form of equation A7.4.

It is now possible to use equation A7.17 in the evaluation of certain temperature dependent properties of the electron gas.

(i) TO FIND THE FERMI ENERGY AT TEMPERATURE $T$

The Fermi energy $\epsilon_F(0)$ at absolute zero has already been defined in equation 5.15. The Fermi energy $\epsilon_F$ at temperature $T$ is defined by the condition imposed by equation 5.13*a*, namely

$$N = \int_0^\infty n(\epsilon)\,d\epsilon = \int_0^\infty f(\epsilon)g(\epsilon)\,d\epsilon \qquad 5.13a$$

If $g(\epsilon)$ is substituted for $\phi(\epsilon)$ in equation A7.17 and $I$ is set equal to $N$, this condition gives

$$N = \int_0^{\epsilon_F} g(\epsilon)\,d\epsilon + g'(\epsilon_F)(kT)^2\frac{\pi^2}{6} \qquad \text{A7.18}$$

Remembering that equation 5.13*b* gives $N = \int_0^{\epsilon_F(0)} g(\epsilon)\,d\epsilon$ equation A7.18 may be rewritten so that

$$g'(\epsilon_F)(kT)^2\frac{\pi^2}{6} = \int_0^{\epsilon_F(0)} g(\epsilon)\,d\epsilon - \int_0^{\epsilon_F} g(\epsilon)\,d\epsilon$$

$$= \int_{\epsilon_F}^{\epsilon_F(0)} g(\epsilon)\,d\epsilon \qquad \text{A7.19}$$

Since the difference between $\epsilon_F$ and $\epsilon_F(0)$ is small, it is a good approximation to write $\int_{\epsilon_F}^{\epsilon_F(0)} g(\epsilon)\,d\epsilon \simeq g(\epsilon_F(0))(\epsilon_F(0) - \epsilon_F)$ so that equation A7.19 becomes

$$g'(\epsilon_F)(kT)^2\frac{\pi^2}{6} = g(\epsilon_F(0))(\epsilon_F(0) - \epsilon_F) \qquad \text{A7.20}$$

Now, by equation 5.14, $g(\epsilon) = 4\pi V\left\{\frac{2m}{h^2}\right\}^{\frac{3}{2}}\epsilon^{\frac{1}{2}}$ so that

$$g'(\epsilon) = 4\pi V\left\{\frac{2m}{h^2}\right\}^{\frac{3}{2}}\frac{\epsilon^{-\frac{1}{2}}}{2} = \tfrac{1}{2}\frac{g(\epsilon)}{\epsilon}$$

Equation A7.20 then becomes

$$\frac{g(\epsilon_F)}{\epsilon_F}(kT)^2\frac{\pi^2}{12} = g(\epsilon_F(0))(\epsilon_F(0) - \epsilon_F) \qquad \text{A7.21}$$

Again because $\epsilon_F \simeq \epsilon_F(0)$ for $kT \ll \epsilon_F$ it is possible to write $\frac{g(\epsilon_F)}{\epsilon_F} \simeq \frac{g(\epsilon_F(0))}{\epsilon_F(0)}$ with negligible error so that equation A7.21 gives

$$\frac{(kT)^2}{\epsilon_F(0)}\frac{\pi^2}{12} = \epsilon_F(0) - \epsilon_F \qquad \text{A7.22}$$

and

$$\epsilon_F = \epsilon_F(0))\left\{1 - \frac{(kT)^2}{\epsilon_F(0)^2}\frac{\pi^2}{12}\right\}$$

or

$$\boxed{\epsilon_F = \epsilon_F(0)\left[1 - \frac{\pi^2}{12}\left(\frac{T}{T_F}\right)^2\right]} \qquad \text{A7.23}$$

It is the fact that the "correction term" $\frac{\pi^2}{12}\left(\frac{T}{T_F}\right)^2$ is almost negligible compared with unity which generally allows the substitution of $\epsilon_F(0)$ for $\epsilon_F$ to be made without the introduction of any measurable error.

(ii) THE ENERGY OF THE ELECTRONS AS A FUNCTION OF TEMPERATURE

The total energy of an electron gas can be written as

$$E = \int_0^\infty \epsilon n(\epsilon)\, d\epsilon$$

$$= \int_0^\infty \epsilon f(\epsilon) g(\epsilon)\, d\epsilon \qquad \text{A7.24}$$

The evaluation of this integral with the aid of equation A7.17 may be carried out using the substitution of $\epsilon g(\epsilon)$ for $\phi(\epsilon)$ and $E$ for $I$. Then, with $\phi'(\epsilon_F)$ replaced by $(g(\epsilon_F)+\epsilon_F g'(\epsilon_F))$, equation A7.24 becomes

$$E = \int_0^{\epsilon_F} \epsilon g(\epsilon)\, d\epsilon + (g(\epsilon_F)+\epsilon_F g'(\epsilon_F))(kT)^2 \frac{\pi^2}{6} \qquad \text{A7.25}$$

Again it is possible to use the fact that $\epsilon_F \simeq \epsilon_F(0)$ and $g(\epsilon_F) \simeq g(\epsilon_F(0))$ to give

$$\begin{aligned}\int_0^{\epsilon_F} \epsilon g(\epsilon)\, d\epsilon &= \int_0^{\epsilon_F(0)} \epsilon g(\epsilon)\, d\epsilon - \int_{\epsilon_F}^{\epsilon_F(0)} \epsilon g(\epsilon)\, d\epsilon \\ &= E(0) - \epsilon_F(0) g(\epsilon_F(0))(\epsilon_F(0) - \epsilon_F) \qquad \text{A7.26}\end{aligned}$$

where $E(0)$ is the total energy of the electrons at $T = 0$. Using the value of $(\epsilon_F(0)-\epsilon_F)$ given by equation A7.22, equation A7.26 becomes

$$\int_0^{\epsilon_F} \epsilon g(\epsilon)\, d\epsilon = E(0) - g(\epsilon_F(0))(kT)^2 \frac{\pi^2}{12} \qquad \text{A7.27}$$

Now, in equation A7.25, it is possible to write

$$g(\epsilon_F)+\epsilon_F g'(\epsilon_F) = \tfrac{3}{2} g(\epsilon_F) \simeq \tfrac{3}{2} g(\epsilon_F(0))$$

where use has again been made of the relationship $g'(\epsilon) = \frac{1}{2}[g(\epsilon)]/\epsilon$ and the fact that the temperature dependent terms are small. Then, on substituting from equation A7.27 in equation A7.25, the total energy is

$$\begin{aligned}E &= E(0) - g(\epsilon_F(0))(kT)^2 \frac{\pi^2}{12} + \tfrac{3}{2} g(\epsilon_F(0))(kT)^2 \frac{\pi^2}{6} \\ &= E(0) + g(\epsilon_F(0))(kT)^2 \frac{\pi^2}{6} \qquad \text{A7.28}\end{aligned}$$

The mean energy of the electrons at absolute zero is given by equation 5.17 as $\frac{3}{5}\epsilon_F(0)$ so that $E(0) = \frac{3}{5} N \epsilon_F(0)$. Also, since $g(\epsilon) =$ (constant) $\times \epsilon^{\frac{1}{2}}$, $N = \int_0^{\epsilon_F(0)} g(\epsilon)\, d\epsilon = \frac{2}{3}\epsilon_F(0) g(\epsilon_F(0))$, so that $g(\epsilon_F(0)) = \frac{3}{2}\frac{N}{\epsilon_F(0)}$. Thus equation A7.28 may be written

$$\boxed{E = N\left[\tfrac{3}{5}\epsilon_F(0) + \frac{(kT)^2}{\epsilon_F(0)}\frac{\pi^2}{4}\right]} \qquad \text{A7.29}$$

The corresponding mean energy of the electrons is

$$\bar{\epsilon} = \frac{E}{N} = \epsilon_F(0)\left[\tfrac{3}{5} + \frac{\pi^2}{4}\left(\frac{T}{T_F}\right)^2\right] \qquad \text{A7.30}$$

(iii) THE ELECTRONIC SPECIFIC HEAT

The specific heat of the electron gas is obtained by differentiating the expression for the total energy given by equation A7.29 with respect to the temperature. Keeping the volume constant so that $\epsilon_F(0)$ is unchanged gives

$$C_v = \left\{\frac{\partial E}{\partial T}\right\}_V = \frac{\pi^2}{2}\frac{Nk^2T}{\epsilon_F(0)}$$

For "one gramme atom" of electron gas $N$ will be Avogadro's number and, with $\epsilon_F(0) = kT_F$, the specific heat becomes

$$C_v = \frac{\pi^2}{2}\frac{RT}{T_F} \qquad \text{A7.31}$$

where $R$, the universal gas constant, is written in place of $N_A k$.

(It must be noted by the student that, in general, the approximations introduced into the mathematical treatment in this appendix will result in errors much too small to be distinguished by the experimental measurements.)

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